Antiferromagnetism in a Family of $S = 1$ Square Lattice Coordination Polymers NiX$_2$(pyz)$_2$ ($X = \text{Cl}, \text{Br}, \text{I}, \text{NCS}$; pyz = Pyrazine)

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ABSTRACT: The crystal structures of NiX$_2$(pyz)$_2$ ($X = \text{Cl} (1), \text{Br} (2), \text{I} (3),$ and NCS (4)) were determined by synchrotron X-ray powder diffraction. All four compounds consist of two-dimensional (2D) square arrays self-assembled from octahedral NiN$_4$X$_2$ units that are bridged by pyz ligands. The 2D layered motifs displayed by 1−4 are relevant to bifluoride-bridged [Ni(HF$_2$)(pyz)$_2$]EF$_6$ ($E = \text{P, Sb}$), which also possess the same 2D layers. In contrast, terminal $X$ ligands occupy axial positions in 1−4 and cause a staggered packing of adjacent layers. Long-range antiferromagnetic (AFM) order occurs below 1.5 (Cl), 1.9 (Br and NCS), and 2.5 K (I) as determined by heat capacity and muon-spin relaxation. The single-ion anisotropy and $g$ factor of 2, 3, and 4 were measured by electron-spin resonance with no evidence for zero-field splitting (ZFS) being observed. The magnetism of 1−4 spans the spectrum from quasi-two-dimensional (2D) to three-dimensional (3D) antiferromagnetism. Nearly identical results and thermodynamic features were obtained for 2 and 4 as shown by pulsed-field magnetization, magnetic susceptibility, as well as their Néel temperatures. Magnetization curves for 2 and 4 calculated by quantum Monte Carlo simulation also show excellent agreement with the pulsed-field data. Compound 3 is characterized as a 3D AFM with the interlayer interaction ($J_{\perp}$) being slightly stronger than the intralayer interaction along Ni−pyz−Ni segments ($J_{\text{pyz}}$) within the two-dimensional [Ni(pyz)$_2$]$^{2+}$ square planes. Regardless of $X$, $J_{\text{pyz}}$ is similar for the four compounds and is roughly 1 K.

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1. INTRODUCTION

Low-dimensional Ni(II)-based $S = 1$ quantum antiferromagnets continue to draw much interest from the condensed matter science community. Since Haldane$^{1,2}$ predicted that an antiferromagnetic Heisenberg chain has a singlet ground state and a finite gap to the lowest excited state for integer spins, this conjecture has inspired numerous studies of $S = 1$ antiferromagnets in low dimensions. While most of the work done so far is related to one-dimensional (1D) models or quasi-one-dimensional (Q1D) compounds, less work has been performed on two-dimensional models (2D) or quasi-two-dimensional (Q2D) compounds$^{12-15}$ partially due to the difficulty in applying theoretical/numerical techniques to these models. In low-dimensional $S = 1$ antiferromagnets, the nature of the ground state can be strongly modified by the spatial dimensionality as well as the zero-field splitting (ZFS) of 3$d^8$ Ni(II),$^{16}$ both of which can be tuned by chemical synthesis. In addition, the presence of two orthogonal magnetic orbitals in octahedrally coordinated Ni(II), $d_{x^2-y^2}$ and $d_{x^2-y^2}$, affords multiple options for forming spin exchange pathways, allowing flexibility in tuning the magnetic dimensionality via crystal engineering.

We and others have been developing two-dimensional Cu(II)-based square lattices comprised of pyrazine (pyz) bridges. Among these are $[\text{Cu}(\text{HF})_2(\text{pyz})_2]Z (Z = \text{BF}_4^-$, $\text{PF}_6^-$, $\text{SbF}_6^-$ and $\text{TaF}_6^-$),$^{17-20}$ $[\text{Cu}(\text{ClO}_4)_2(\text{pyz})_2]^-$, $[\text{Cu}(\text{BF}_4)_2(\text{pyz})_2]^-$, and $[\text{Cu}(\text{pyz})_2(\text{pyO})_2](\text{PF}_6)_2$,$^{25}$ which all display long-range order ($\text{LRO}$) between 1.5 and 4.3 K. The square $[\text{Cu}(\text{pyz})_2]^-$ planes in $[\text{Cu}(\text{HF})_2(\text{pyz})_2]Z$ are connected by $\text{BF}_4^-$ bridges to afford three-dimensional (3D) frameworks with $Z$ occupying the interior sites. However, the magnetism is very two-dimensional as a result of very weak couplings through Cu–FHF–Cu bonds$^{25}$ due to limited overlap between the fluorine $p_z$ orbital and the magnetic orbital of Cu(II), $d_{x^2-y^2}$, lying in the $[\text{Cu}(\text{pyz})_2]^-$ planes.$^{26}$ The last three examples above contain axial ClO$_4^-$, BF$_4^-$, or pyO ligands, and the 2D layers stack in a staggered fashion. Extension of some of this work to include Ni(II) has proven to be more challenging, as growth of single crystals is difficult. As such, implementation of synchrotron X-ray diffraction to determine crystal structures, including those described here, has been crucial to our characterization efforts.

In addition, the $\text{A}_2$ ground state of an octahedrally coordinated Ni(II) ion is magnetically more complex than Cu(II) owing to the presence of ZFS induced by spin–orbital couplings. The effective spin Hamiltonian ($S = 1$) is given by

\[
\hat{H} = \sum_{(i)} D(S_i^{z^2}) + \sum_{(ij)} J_{ij} S_i^z S_j^z
\]  

(1)

Experimentally, it becomes challenging to distinguish between the effects from magnetic exchange interactions ($J_{ij}$) and single-ion ZFS ($D$), especially when polycrystalline samples are involved.$^{27}$ The difficulty lies in the fact that, in many circumstances, magnetometry data can be fitted to several models with different combinations of $D$ and $J_{ij}$, which makes it challenging to characterize a system unambiguously. In such a case, additional spectroscopic measurements are required to constrain the parameters in the Hamiltonian.

Considering these challenges, we recently described the structural, electronic and magnetic properties of $[\text{Ni}(\text{HF})_2(\text{pyz})_2]Z (Z = \text{PF}_6^-$, $\text{SbF}_6^-$).$^{27,28}$ Interestingly, $Z = \text{PF}_6^-$ exists as two isostructural polymorphs with similar 3D structural motifs; the $\alpha$-phase is monoclinic, while the $\beta$-phase is tetragonal and isostructural to the equivalent Cu(II) compound. A spatial exchange anisotropy was found in these materials due to the presence of coexisting Ni–FHF–Ni ($J_{\text{FHF}}$) and Ni–pyz–Ni pathways ($J_{\text{pyz}}$), where $|J_{\text{FHF}}| > |J_{\text{pyz}}|$. The dominant Ni–FHF–Ni pathways allowed us to interpret the $\chi(T)$ data according to a Q1D chain model above $T_{\text{max}}$, but it was not possible to experimentally determine $J_{\text{pyz}}$ owing to the polycrystalline nature of the samples. Density-functional theory (DFT) confirmed the magnetic exchange properties of these systems and that $J_{\text{pyz}}$ was indeed much smaller than $J_{\text{FHF}}$.

Angular overlap model (AOM) analyses of UV–vis spectroscopic data determined $D$ to be $-7.5$ K ($\alpha$–$\text{PF}_6^-$), $10.3$ K ($\beta$–$\text{PF}_6^-$), and $11.2$ K ($\text{SbF}_6^-$). The corresponding high Néel temperatures ($T_N$ the onset of long-range antiferromagnetic order) of 6.2, 7.0, and 12.2 K suggest that $J_{\text{pyz}}$ must be larger than that calculated, or alternatively, the magnetic orders are assisted by $D$. In order to address these scenarios as well as to find $J_{\text{pyz}}$ quantitatively, analogous model compounds based on weakly interacting 2D $[\text{Ni}(\text{pyz})_2]^2$ square lattices are required for comparison.

Four compounds with similar $[\text{Ni}(\text{pyz})_2]^2$ square lattices were synthesized and studied: $\text{NiCl}_2(\text{pyz})_2$ (1), $\text{NiBr}_2(\text{pyz})_2$ (2), NiI$_2$(pyz)$_2$ (3), and $\text{Ni(NCS)}_2(\text{pyz})_2$ (4). Some of them, notably 1, 2, and 4, were synthesized and spectroscopically characterized several years ago,$^{29-32}$ although their crystal structures were not explicitly determined. More recently, the structure of 2 was determined by powder neutron diffraction and found to be consistent with the hypothetical square lattice structure.$^{33}$

Compound 3 is described here for the first time. The related Ni(II) compound, 4, reportedly exists in two polymorphic forms; however, as will be described below, we find evidence for only one of the two phases in our samples.

As for the magnetic properties of 1–4, the temperature dependence of the magnetic susceptibility data, $\chi(T)$, for 1 and 2 have been reported ($T \geq 5$ K),$^{32,33}$ while those for 3 and 4 have not. The analysis of the $\chi(T)$ data for 1 and 2 gave $D = 7.92$ and 14.8 K, respectively. Furthermore, these studies also suggested that magnetic couplings along Ni–pyz–Ni were probably very week. An estimate of $J_{\text{pyz}}$ was made by employing a mean-field contribution, giving $g_f = 0.39$ K for 2 ($g_f = 0.95$ K for 2).$^{32,33}$

In this work, we have carried out an extensive experimental and theoretical investigation of 1–4, employing modern instrumental methods to characterize their structural as well as temperature- and field-dependent magnetic properties. Our interpretation of the experimental results suggests the interlayer magnetic couplings in 1–4 are significantly suppressed compared to the $[\text{Ni}(\text{HF})_2(\text{pyz})_2]^2Z$ compounds and become comparable or less than $J_{\text{pyz}}$. To clarify the possible Ni(II) ZFS contribution to the magnetism, electron spin resonance measurements were performed on 1–4. $J_{\text{pyz}}$ in 2–4 is quantitatively determined within the picture of Q2D magnetism, and the conclusions are supported by quantum Monte Carlo (QMC) calculations. The common $[\text{Ni}(\text{pyz})_2]^2$ square lattices exhibited by 1–4 are relevant to establishing magnetostuctural correlations in the metal–organic frameworks, $[\text{Ni}(\text{HF})_2(\text{pyz})_2]^2Z (Z = \text{PF}_6^-$ and $\text{SbF}_6^-)$.

2. EXPERIMENTAL METHODS

**Syntheses.** Following a general procedure, 1 and 2 were prepared as powders using a fast precipitation reaction between the corresponding NiX$_2$, pyz, and two equivalents of pyrazine. Each reagent was dissolved in 3 mL of H$_2$O and quickly mixed together while stirring. For 4, KNCS (2.16 mmol, 0.2100 g) and pyz (2.16 mmol, 0.1730 g) were dissolved together in 5 mL of H$_2$O. To this solution was added, while stirring, Ni(NO$_3$)$_2$·9H$_2$O (1.08 mmol, 0.1973 g) to afford a pale blue precipitate.
Inorganic Chemistry

In all instances, the powders were isolated by suction filtration, washed with H₂O, and dried in vacuo for ∼2 h. Compound 3 was prepared via a mechanochemical reaction involving grinding of NiI₂ (2.88 mmol, 0.9013 g) with an excess of pyrazine (6.78 mmol, 0.2307 g). A Parr acid-digestion bomb was charged with the reaction mixture and placed inside a temperature programmable oven which was set at a temperature of 403 K. The sample was held isothermal for 2 weeks and then allowed to cool slowly to room temperature, at which time a homogeneous orange-brown solid had formed. The final product was obtained by washing the sample with fresh diethyl ether to remove any unreacted pyz. All four compounds were highly pure and isolated in yields exceeding 90%.

Structural Determinations. For NiX₂(pyz)₂ (X = Cl, Br or NCS), high resolution synchrotron powder X-ray diffraction patterns were collected at the X12A and X16C beamline at the National Synchrotron Light Source at Brookhaven National Laboratory. X-rays of a particular wavelength were selected using a Si(111) channel cut monochromator. Behind the sample, the diffracted beam was analyzed with a Ge(111) crystal and detected by a NaI scintillation counter. Wavelength and diffractometer zero were calibrated using a sample of NIST Standard Reference Material 1976, a sintered plate of Al₂O₃. The sample was loaded into a 1.0-mm-diameter glass capillary and flame-sealed.

For NiI₂(pyz)₂, high resolution synchrotron powder X-ray diffraction data were collected using beamline 11-BM at the Advanced Photon Source (APS). Discrete detectors are scanned over a 34° range in 2θ with data points collected every 0.001° using a scan speed of 0.01°/s. Data were collected while continually scanning the diffractometer 2θ-arm.

Indexing was performed in TOPAS Academic,77,38 and space groups were tentatively assigned through systematic absences to be I4/m/mmm for NiX₂(pyz)₂ (X = Cl, Br, or I) and C2/m for Ni(NCS)₂(pyz)₂. The I4/m/mmm space group was also reported for NiBr₂(pyz)₂ in ref 33. From the space group assignment and stoichiometric contents, it was possible to place the Ni on the corresponding 2a (0, 0, 0) special position. The remaining atomic positions were determined by simulated annealing in TOPAS Academic. From these initial models, these structures were successfully refined to determine more precise atomic positions. Pyrazine hydrogens were placed on ideal geometrically determined positions.

Magnetic Measurements. Magnetization (M) versus temperature data were collected (and converted to susceptibility by the relation χ(T) = M/H) on a Quantum Design MPMS 7 T SQUID. Powder samples of 1–4 were loaded into gelatin capsules, mounted in a plastic drinking straw, and affixed to the end of a stainless steel/brass rod. The sample was cooled in zero-field to a base temperature of 2 K, the magnet charged to 0.1 T, and data taken upon warming to 300 K.

Pulsed Fields. M(R) measurements (up to 60 T) made use of a 1.5-mm-bore, 1.5-mm-long, 1500-turn-compensated coil susceptometer, constructed from a 50 gauge high-purity copper wire. When the 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 ampule 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 He cryostat providing a base temperature of 0.5 K. The field B was measured by integrating the voltage induced in a 10-turn coil calibrated by observing the de Haas–van Alphen oscillations of the belt orbits of the copper coils of the susceptometer.

Heat Capacity. Cᵥ measurements were carried out on polycrystalline samples of 1–4 by means of two independent techniques; the traditional relaxation79 and dual-slope methods.80 In the relaxation method, the heat pulse was applied to the sample heater, and the resultant exponential temperature decay with a small temperature step, which is ~3% of the thermal bath temperature, was observed. The Cᵥ at a single temperature was evaluated by the time constant of the decay curve and the thermal conductance of the thermal link. In the dual slope method, the sample was heated and subsequently cooled through a broad temperature range, and the Cᵥ(T) in the wide temperature range was evaluated using both heating and cooling curves. This method allows quick collection of a large amount of Cᵥ(T) data, which is important in determining the transition temperature at several magnetic fields. However, it requires an excellent thermal contact between the sample and the thermometer that can only be used in cases of minimal tau-2 effects; i.e., the thermal relaxation between the sample and the platform must be fast. For this reason, Cᵥ(T) of 1 was obtained by traditional relaxation method only. For 4, using the same setup as the Cᵥ experiments, we additionally observed a magnetocaloric effect (MCE) by sweeping the magnetic field at 1 T/min. This method measures the entropy change as a function of magnetic field and can detect phase boundaries with cooling and heating responses. These Cᵥ(T) and MCE measurements were performed on 2.910, 1.479, 2.284, and 3.406 mg of 1, 2, 3, and 4, respectively. The powders were mixed with a small amount of Apeizon-N grease and pressed between Si plates to obtain good temperature homogeneity. Compounds 1, 2, and 4 were measured in an Oxford 15 T superconducting magnet system capable of reaching a base temperature of 0.4 K. Compound 3 was measured in a 9 T Quantum Design Physical Property Measurement System. The addenda specific heats due to Apeizon-N grease, Si plates, and sample platform were measured separately. After subtracting the addenda contribution from the total specific heat, the specific heat of the sample was obtained. Excellent agreement (within ~5%) between the two Cᵥ(T) techniques was confirmed for 2 and 4.

Muon-Spin Relaxation. Zero-field muon-spin relaxation (ZF μSR) measurements were made on polycrystalline samples of 1–4 using the general purpose surface (GPS) spectrometer at the Swiss Muon Source (1 and 2) and the EMU (1), MuSR (3), and ARGUS (4) instruments at the STFC ISIS facility. For the measurement, the samples were mounted in silver foil packets onto silver backing plates.

In a μSR experiment,82 spin-polarized positive muons are stopped in a target sample, where the muon usually occupies an interstitial position in the crystal. The observed property in the experiment is the time evolution of the muon spin polarization, the behavior of which depends on the local magnetic field at the muon site. Each muon decays, with an average lifetime of 2.2 μs, into two neutrinos and a positron, the latter particle being emitted preferentially along the instantaneous direction of the muon spin. Recording the time dependence of the positron emission directions therefore allows the determination of the spin-polarization of the ensemble of muons. In our experiments, positrons are detected by detectors placed forward (F) and backward (B) of the initial muon polarization direction. Histograms N_F(t) and N_B(t) record the number of positrons detected in the two detectors as a function of time following the muon implantation. The quantity of interest is the decay positron asymmetry function, defined as

\[
A(t) = \frac{N_F(t) - \alpha_{av} N_B(t)}{N_F(t) + \alpha_{av} N_B(t)}
\]

where α_{av} is an experimental calibration constant. A(t) is proportional to the spin polarization of the muon ensemble.

Electron Spin Resonance (ESR). D-band (130 GHz) ESR measurements were performed on powder samples of 1–3. A phase-locked dielectric resonator oscillator in conjunction with a series of IMPATT diodes was used as the microwave source and detector. A field modulation was employed for D-band ESR measurements. Multi-high-frequency EPR measurements were also performed on a powder sample of 2–4 using a cavity perturbation technique spanning the frequency range from 40 to 170 GHz. A millimeter-vector-network analyzer served as the microwave source and detector. ESR measurements were performed in a 6 T horizontal-bore superconducting magnet with the temperature regulated between 1.5 and 300 K using a helium gas flow cryostat.

Quantum Monte Carlo Calculations. Numerical calculations of the spin-1 antiferromagnetic Heisenberg model in an applied magnetic field were performed using the stochastic series expansion quantum Monte Carlo (QMC) method with directed loop updates.83 For antiferromagnetic exchange interactions, sublattice rotation is required to avoid the sign problem in QMC. By taking the direction of the applied magnetic field as the discretization axis, sublattice rotation on a bipartite lattice leads to a sign-problem-free Hamiltonian as long as the applied
field is parallel or perpendicular to the axis of exchange anisotropy. The case of applied field parallel to the axis of exchange anisotropy has been well-studied. For the case of perpendicular applied fields, we use a slightly modified approach to account for a lack of the usual conservation law.44

Density Functional Theory (DFT). Computational modeling was performed on dinuclear entities using the structural data from X-ray determinations. Evaluation of the exchange couplings was based on the broken-symmetry (BS) approach of Noodleman45 as implemented in the ORCA version 2.8 suite of programs.46–48 The formalism of Yamaguchi et al., which employs calculated expectation values $\langle S^2 \rangle$ for both high-spin and broken-symmetry states, was used.49,50 Calculations related to magnetic interactions have been performed using the PBE0 functional. The def2-TZVP basis set from Ahlrichs was used.51

3. RESULTS

A. Crystal Structures. Crystallographic refinement details as well as selected bond lengths and bond angles for 1–4 are listed in Tables 1 and 2. The data correspond to room temperature (1, 2, and 4) and 100 K (3) structures.

NiCl$_2$(pyz)$_2$ (1), NiBr$_2$(pyz)$_2$ (2), and NiI$_2$(pyz)$_2$ (3). The atom labeling scheme is shown in Figure 1a. Compounds 1–3 are isomorphous and consist of tetragonally elongated NiX$_2$N$_4$ sites, with the axial sites being occupied by the bulkier X anions. The Ni–N distances are only slightly perturbed by X (2.145(2) Å (1), 2.131(4) Å (2), and 2.133(1) Å (3)), whereas the Ni–X bond lengths are substantially longer at 2.400(1) Å (1), 2.5627(9) Å (2), and 2.7919(1) Å (3) due to increasing ionic radius of the halide. The Ni–N distances in 1–3 are similar to those reported in other compounds with Ni–pyz–Ni bridges.52–55 However, the axial bonds (Ni–X) in 1–3 are significantly longer than those in compounds with related structures that contain either 1D or 2D Ni–pyz–Ni bridges. This is likely due to the relatively large radius of the halogen atoms in 1–3 comparing the axial ligands in other systems which contain smaller O- or N-donor atoms. The topological structures of 1–3 can be described as infinite 2D square lattices with NiX$_2$N$_4$ octahedra bridged by pyz linkages along the $a$ and $b$ axes (Figure 2a) to afford perfectly linear Ni–N–N trajectories.

A 2-fold positional disorder of the pyz ligands occurs as a result of the mirror planes in the $14/mmm$ space group (Figure 2b). The small unit cell is consistent with this disorder. To have an ordered arrangement such that adjacent pyz ligands adopt a propeller-like disposition around the Ni(II) center would require a larger unit

| Table 1. Crystallographic Refinement Parameters for 1–4 As Determined by Synchrotron X-Ray Powder Diffraction |
| --- |
| **compound** | **NiCl$_2$(pyz)$_2$ (1)** | **NiBr$_2$(pyz)$_2$ (2)** | **NiI$_2$(pyz)$_2$ (3)** | **Ni(NCS)$_2$(pyz)$_2$ (4)** |
| emp. formula | C$_2$N$_4$H$_6$NiCl$_2$ | C$_2$N$_4$H$_6$NiBr$_2$ | C$_2$N$_4$H$_6$NiI$_2$ | C$_2$N$_4$H$_6$NiS$_2$ |
| wt. (g/mol) | 289.77 | 378.67 | 472.68 | 335.03 |
| $T$ (K) | | 100 | 298 |
| crystal class | tetragonal | tetragonal | tetragonal | monoclinic |
| space group | $14/mmm$ | $14/mmm$ | $14/mmm$ | $C2/m$ |
| $a$ (Å) | 7.0425(2) | 7.0598(2) | 7.05750(2) | 7.05750(2) |
| $b$ (Å) | 7.0425(2) | 7.0598(2) | 7.05750(2) | 7.05750(2) |
| $c$ (Å) | 10.7407(3) | 11.3171(3) | 12.25594(5) | 7.2772(2) |
| $\alpha$ (deg) | 90 | 90 | 90 | 118.623(2) |
| $\beta$ (deg) | 90 | 90 | 90 | 90 |
| $\gamma$ (deg) | 90 | 90 | 90 | 90 |
| $\rho$ (Å) | 1.471 | 1.093 | 1.431 | 1.720 |
| $\mu$ (g/cm$^3$) | 1.807 | 2.231 | 2.571 | 1.729 |
| $\lambda$ (Å) | 0.699973 | 0.754056 | 0.41574 | 0.6984 |
| $\tilde{\omega}_y$ | 0.05592 | 0.04524 | 0.05248 | 0.04531 |
| $\tilde{\omega}_y$ | 0.06987 | 0.05449 | 0.03249 | 0.05644 |
| $\chi$ | 1.471 | 1.093 | 1.431 | 1.720 |

| Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for 1–4 |
| --- |
| **NiCl$_2$(pyz)$_2$ (1)** |
| Ni1–Ni1 | 2.145(2) | Ni1–Cl1 | 2.400(1) |
| Ni1–C1 | 1.336(2) | N1–Ni1–Cl1 | 90° |
| Ni1–Ni1–Cl1 | 180° | N1–Ni1–N1 | 90° |
| Ni1–N1–C1 | 120.5(1)° | dihedral angle | 47.4(2)° |
| **NiBr$_2$(pyz)$_2$ (2)** |
| Ni1–Ni1 | 2.131(4) | Ni1–Br1 | 2.5627(9) |
| Ni1–C1 | 1.351(1) | N1–Ni1–Br1 | 90° |
| Br1–Ni1–Br1 | 180° | N1–Ni1–N1 | 90° |
| Ni1–N1–C1 | 121.4(2)° | dihedral angle | 46.5(2)° |
| **NiI$_2$(pyz)$_2$ (3)** |
| Ni1–Ni1 | 2.135(1) | Ni1–I1 | 2.7919(9) |
| Ni1–C1 | 1.349(1) | N1–Ni1–I1 | 90° |
| Ni1–Ni1 | 180° | N1–Ni1–N1 | 90° |
| Ni1–N1–C1 | 121.4(2)° | dihedral angle | 45.8(1)° |
| **Ni(NCS)$_2$(pyz)$_2$ (4)** |
| Ni1–Ni1 | 2.020(5) | Ni1–N2 | 2.184(3) |
| Ni1–C1 | 1.184(7) | N2–C2 | 1.303(3) |
| S1–C1 | 1.591(5) | C2–C3 | 1.401(5) |
| Ni1–C2–S1 | 175.5(7)° | N1–Ni1–C1 | 163.5(3)° |
| Ni1–N1–N2 | 88.4(2)° | N1–Ni1–N1 | 180° |
| Ni2–N2–C2 | 180° | dihedral angle | 65.3(2)° |

*Measured as the pyz tilt angle relative to the ab-plane.

Figure 1. Room temperature asymmetric units and atom labeling schemes for (a) NiCl$_2$(pyz)$_2$ (1) and (b) Ni(NCS)$_2$(pyz)$_2$ (4). The asymmetric units and atom labeling schemes for NiBr$_2$(pyz)$_2$ (2) and NiI$_2$(pyz)$_2$ (3) are similar to those of 1 with the Cl atom being replaced by Br or I for 2 and 3, respectively.
the Ni(II) ion of a given lattice lies above/below the centers of neighboring square lattices (Figure 2b). The bulky X anions act as spacers to separate each layer, giving interlayer Ni···Ni separations of 7.32 Å (1), 7.54 Å (2), and 7.90 Å (3). It should be noted that the 2D structural motif was anticipated based on early infrared spectroscopic evidence \(^{31,32}\) and now confirmed here using X-ray structural data.

It is worth mentioning that two structures were previously reported for the Co-congener of 1, CoCl\(_2\)\(\text{pyz}\)\(_2\). The far-infrared spectra for CoCl\(_2\)\(\text{pyz}\)\(_2\) suggested tetragonal symmetry (\(I4/mmm\)), \(^{32}\) whereas a later single crystal X-ray study indicated an orthorhombic space group \(Ccma\). \(^{33}\) Both structures consist of a square lattice motif with Co(II) centers bridged by pyz ligands. For the sake of comparison, the high-intensity synchrotron X-ray diffraction data for 1–3 were also fitted against the \(Ccma\) space group, but poor agreement was found as several calculated intensities were either split or completely missing from the experimental data. A similar detailed structural study of 2 also indicated preference for \(I4/mmm\). \(^{33}\) From our work, we conclude that the \(I4/mmm\) space group is the appropriate choice for these materials, at least, as prepared using our synthetic methodology.

\(\text{Ni(NCS)}_2\)\(\text{pyz}\)\(_2\) (4). Previously, two different structural modifications have been reported, each having monoclinic symmetry (\(C2/m\) and \(P2_1/n\)) at 293 K. \(^{34,35}\) Although both structures possess octahedral Ni(II) centers, four pyz ligands in the equatorial plane, two axial NCS\(^-\) ligands and 2D layered motifs that consist of orthogonally cross-linked Ni–pyz–Ni chains, an essential difference between them lies in the relative distortion of the Ni\(_{6}\) octahedron. In the \(C2/m\) structure as described by Wriedt et al. \(^{34}\) four equivalent Ni–N\(_{\text{pyz}}\) bonds [2.162(1) Å] occupy the 2D plane while the axial direction contains shorter Ni–N bonds [2.033(2) Å]. In contrast, three distinct pairs of Ni–N distances are found in the \(P2_1/n\) variant, with an axial elongation along one of the Ni–pyz–Ni chains [Ni–N\(_{\text{pyz}}\) = 2.440(3) Å]. The other two Ni–N bonds contain the other (orthogonal) Ni–pyz–Ni chain, whereas the Ni–N bonds (from the NCS\(^-\) ligand) are 1.945(3) Å. The strong elongation of the six-coordinate Ni(II) center is at odds with expectations especially since Jahn–Teller distortion is not possible for a 3d\(^8\) ion.

For the sake of a careful structural and magnetic comparison to 1–3, we have re-examined the 298 K structure of 4 using high-resolution synchrotron powder X-ray diffraction. We found the crystal structure of 4 to be essentially identical to that of the reported \(C2/m\) phase and describe the structure in detail here as it is pertinent to the development of magnetostuctural correlations.

Indeed, 4 features four equivalent Ni–N2 (from pyz) bond distances of 2.184(3) Å while Ni–N1 (from NCS\(^-\)) bonds are shorter at 2.020(5) Å. These Ni–N distances are significantly different to the \(P2_1/n\) phase. Other striking variations are observed in the bond angles about the Ni\(_{6}\) octahedron. The main structural feature of 4 is the planar 2D nearly square grid that propagates in the \(ab\) plane as illustrated in Figure 3a. Here, adjoining orthogonal chains afford equivalent intralayer Ni···Ni separations of 7.123(1) Å along both Ni–pyz–Ni chains. The square exhibits a slight rhombic distortion such that the diagonals vary by 3% (9.926 vs 10.218 Å). Also of importance is that the pyz ligands form slightly nonlinear Ni–pyz–Ni bridges such that the N-donor atoms (N1) of the pyz ring lie just off the Ni···Ni trajectory. The Ni1–N2···N1 backbone has an angle of 177.3\(^\circ\) as compared to the 180° angles found in 1–3. By comparison, the \(P2_1/n\) structure exhibits inequivalent Ni···Ni distances of 6.982(1) Å along the \(a\) axis and 7.668(2) Å along \(b\).

Figure 2. (a) Two-dimensional layer of NiCl\(_2\)\(\text{pyz}\)\(_2\) (1) with axial Cl atoms omitted for clarity. (b) Staggered packing of 2D layers in 1. The positional disorder of the pyz ligands is shown as double pyz rings connecting Ni atoms. NiBr\(_2\)\(\text{pyz}\)\(_2\) (2) and NiI\(_2\)\(\text{pyz}\)\(_2\) (3) are isostructural with 1. The unit cell is indicated by dashed lines. Ni, Cl, N, and C atoms are represented as gray, green, blue, and black spheres, respectively. H atoms are omitted for clarity.
observed in the $C_p$ curves for NiBr$_2$(pyz)$_2$ (2), NiI$_2$(pyz)$_2$ (3), and Ni(NCS)$_2$(pyz)$_2$ (4), respectively. The lattice contributions ($C_{\text{latt}}$) to heat capacities are calculated by fitting the $C_p$ at high temperatures ($\geq 10$ K) using a simple Debye fitting.$^{28}$ After subtracting the lattice contribution, the temperature dependence of magnetic entropy is calculated as shown in the inset to Figure 4, which exhibits the tendency to saturate to $R \ln(3)$ for all four compounds. This suggests that the $C_p$ anomaly stems from the $S = 1$ spin [Ni(II) ions] for 1–4.

The distinct $C_p$ anomalies for 2–4 are attributed to the antiferromagnetic (AFM) LRO of $S = 1$ spins. In low-dimensional antiferromagnets with strong spatial exchange anisotropy, $\lambda$ peaks are suppressed due to the onset of short-range ordering above $T_N$, which reduces the entropy change at the transition to LRO.$^{56}$ The presence of the $\lambda$ peaks indicates that 2–4 are close to 3D antiferromagnets in which the interactions in all directions, i.e., within and between the [Ni(pyz)$_2$]$^{2+}$ layers, are similar. On the other hand, the $C_p$ for NiCl$_2$(pyz)$_2$ (1) shows no sharp peak over the measured $T$ range. The broad $C_p$ peak in 1 can be explained by the thermal excitation among $S = 1$ spin states (Schottky anomaly) and/or low-dimensional spin correlations. Unfortunately, we could not draw an unambiguous conclusion as to the sign or magnitude of $D$ for 1. However, the hypothesized $D$ value (based on ESR and susceptibility measurements) is significantly larger than the exchange interaction between Ni(II) ions (see below). Therefore, the thermal excitation among the $S = 1$ multiplet is expected to have marked contributions to the magnetic heat capacity of 1 at high temperatures. The magnetic contribution ($C_{\text{mag}}$) to the heat capacity for 1 is calculated by subtracting $C_{\text{latt}}$ from $C_p$, as shown in Figure 5a. Below 0.6 K, $C_{\text{mag}}$ can be fitted to the spin-wave excitation, $C_{\text{mag}} \propto T^{d/2n}$, with $d = 2.99(3)$ and $n = 1$ as shown in the inset to Figure 5a. This temperature dependence deviates from that expected for the Schottky anomaly ($C_{\text{mag}} \propto T^{-1} e^{-D/T}$ for $T \ll D$), suggesting the Ni–Ni interactions play an important role at low temperatures (see more in section 3F). The $d$ value obtained from the low temperature fit is very close to the $T^3$ dependence expected for 3D AFM spin waves.$^{60,61}$ Hence, it is possible that 1 goes through a transition to LRO within the experimental temperature range. The lack of a $\lambda$ peak is indicative of the presence of significant spatial exchange anisotropy among the magnetic interactions in 1. In comparing the data for 1 and 2, we predict Q2D magnetism for 1 with $J_{\text{pyz}} > J_1$ (for further

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**Figure 3.** Crystal structure of Ni(NCS)$_2$(pyz)$_2$ (4). (a) A 2D sheet viewed normal to the $ab$ plane where the slight rhombic distortion of the sheet is readily seen. NCS ligands are omitted for clarity. (b) Staggered packing of sheets. The unit cell is indicated by dashed lines. Ni, S, N, and C atoms are represented as gray, dark green, blue, and black spheres, respectively. H atoms are omitted for clarity.

**Figure 4.** Specific heat of polycrystalline samples of NiX$_2$(pyz)$_2$ (X = Cl (1), Br (2), I (3), and NCS (4)). Main panel: zero field heat capacity data collected between 1 and 10 K. The dash lines represent the estimated lattice contribution $C_{\text{latt}}$. Inset: the temperature dependence of the magnetic entropy for 1–4.
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Figure 5. $C_{mag}$ versus $T$ for NiX$_2$(pyz)$_2$ (X = Cl (1), Br (2), I (3), and NCS (4)) under various magnetic fields. The open symbols and solid curves correspond to the data obtained by the traditional relaxation and dual-slope methods, respectively. Inset to a: the low-temperature section curves correspond to the data obtained by the traditional relaxation and the phase boundary extracted by heat capacity and MCE, respectively. The open symbols are extracted by heat capacity and MCE, respectively.

Figure 6. Phase boundary for 2 (○), 3 (△), and 4 (□ and ■) measured by heat capacity and MCE. The open symbols and the solid squares are extracted by heat capacity and MCE, respectively.

C. Search for Long-Range Magnetic Order Using μSR.

Example μSR spectra measured on NiBr$_2$(pyz)$_2$ (2) using the GPS at the Swiss Muon Source are shown in Figure 7. Across the measured temperature range 1.5 $\leq T \leq$ 5 K, we observed monotonic relaxation with no resolvable oscillations in the spectra. (In fact, we found that the spectra for materials 1–3 all share the same form.) The spectra were found to be well described by the function

$$A(t) = A_1 e^{-\lambda_1 t} + A_2 e^{-\lambda_2 t} + A_{bg}$$

(3)

where the initial amplitude $A(0)$ was held fixed. $A_1$ and $A_2$ correspond to the fast and slow relaxing components, respectively. The temperature evolution of the fitted parameters for 2 is shown in Figure 8c and d. In both the spectra (Figure 7) and in the behavior of the fitted parameters (Figure 8c and d), we see a sharp discontinuity on cooling through $T \approx 1.9$ K. This involves a decrease in the amplitude $A_1$ of the slowly relaxing component with relaxation rate $\lambda_2$, implying an increase in the amplitude $A_1$ of the component with relaxation rate $\lambda_1$. The fact that the nonrelaxing component $A_{bg}$ increases sharply implies a transition to a regime with a static distribution of local fields in the sample. This is because those muons whose spins lie parallel to the static local magnetic field at the muon site will not be relaxed and will therefore contribute to the nonrelaxing amplitude $A_{bg}$. In addition, the relaxation rates would be expected...
to be proportional to the second moment of the local magnetic field distribution \( \langle B^2 \rangle \). The rapid increase in relaxation rates \( \lambda_1 \) and \( \lambda_2 \) therefore probably implies an increase in the magnitude of the local magnetic fields at the muon sites. Taken together, these phenomena point toward a transition to a regime of magnetic order taking place at \( T_N = 1.9(1) \) K in 2, which is in reasonable agreement with the peak observed in \( C_p \).

Measurements on NiI\(_2\)(pyz)\(_2\) (3) were made using the MuSR spectrometer at ISIS. The pulsed muon beam at ISIS has a time width \( r \approx 80 \) ns, which limits the time resolution to below \( \sim 1/r \). As a result, we were unable to resolve the fast relaxation (with rate \( \lambda_1 \)) that we considered in the data for material 2, which manifests itself as missing asymmetry. Instead, we plot the slow relaxation rate (Figure 8e) and the baseline asymmetry (\( A_{bg} \)) for \( \lambda_2 \) and \( A_2 \), which show discontinuities upon magnetic ordering around a temperature \( T_N = 2.5(1) \) K, in agreement with the anomaly in the heat capacity.

Measurements were made on Ni(NCS)\(_2\)(pyz)\(_2\) (4) using the ARGUS spectrometer at the ISIS facility. In this case, the spectra showed weak exponential relaxation in the regime \( 0.35 \leq T \leq 4 \) K with no discontinuities observed that would reflect the ordering temperature seen in the heat capacity at \( T_N = 1.8 \) K. It is unclear why the muon should be insensitive to the ordering transition in this material, although we note the possibility of the muon forming bound states with the electronegative NCS\(^-\) and therefore being insensitive to the ordering of the electronic moments. However, this was not the case in Fe(NCS)\(_2\)(pyz)\(_2\) \(^{69}\) where the spectra were of the same form as observed for materials 1−3 where and the magnetic ordering transition was observed.

For measurements made on NiCl\(_2\)(pyz)\(_2\) (1) using the GPS spectrometer, no sharp change in the form of the spectra is observed in the accessible temperature range \( T > 1.5 \) K, although we saw a steep rise in the fast relaxation rate (Figure 8a) as temperature was lowered below 2 K. In order to search for magnetic order in 1, measurements were made down to 0.35 K using a sorption cryostat with the EMU spectrometer at ISIS. As in the case of 1, the ISIS resolution limit prevented us from resolving fast relaxation in this case. Instead, it was instructive to follow \( A_{bg} \) as a function of temperature, shown in Figure 8b. On cooling, we see a sharp decrease below 2 K, leading to a minimum in asymmetry centered around 1.5 K. The decrease in asymmetry on cooling is probably due to the increase in relaxation of the muon spins. This is followed by an increase at lower temperatures probably reflecting a regime where the moments are more static. It is possible that this minimum reflects a magnetic transition in material 1, although the difference in the heat capacity for this compound compared to others in the series means that this is unlikely to be a transition to a regime of long-range magnetic order. Instead, it is possible that the changes in the \( \mu \)SR spectra we observe in the 1.5−2 K region reflect a freezing-out of dynamic relaxation channels causing moments to become more static on the muon (\( \mu s \)) time-scale.

**D. Electron Spin Resonance**

Electron spin resonance (ESR) measurements were performed on powder samples of 1−4 to probe the ZFS and the g factor associated with Ni(II) ions. A thorough search for ESR absorption in NiCl\(_2\)(pyz)\(_2\) (1) at 130 GHz gave no indication for any ESR signal in the temperature range \( 1.9 \leq T \leq 300 \) K, in contrast to 2−4. The lack of ESR signal in 1 is indicative of the presence of a sizable ZFS (\( |D| \geq 6.24 \) K) for 1. The representative ESR spectra for NiBr\(_2\)(pyz)\(_2\) (2) and Ni(NCS)\(_2\)(pyz)\(_2\) (4) at 50 K are shown in Figure 9 and were recorded in the first-derivative mode. A single ESR transition was observed for 2 and 4 up to 6 T. The broad ESR line-width for 2 is likely due to a structural-disorder-induced
were recorded in the transmission mode. The 20 K spectra for 2 and 4 (Figure 10a and c) are consistent with the aforementioned 130 GHz results where a single transition was observed, suggesting $D = 0$ and $g_x = g_y = g_z$. Additional multifrequency ESR measurements were performed on 4 to confirm the absence of $D$ in the compound (inset to Figure 10c). The 15 K spectrum for 3 (Figure 10b) exhibits a broad feature which spreads over the entire field range (6 T). This feature is reminiscent of a spectrum for $g = 2.27(8)$ and $D = 0$ Ni(II) ions. The broad line width associated with the ESR signal of 3 is likely due to $g$-strain/D-strain and/or the presence of non-Heisenberg interactions between Ni(II) ions (see below).

Upon cooling, the ESR resonance fields and line-widths for 2–4 show substantial variations as the temperature approaches the onset of LRO. The temperature-dependence of the spectra above $T_N$ may be attributed to short-range spin correlations. When the temperature approaches $T_N$, it is conceivable that small clusters of spins can be strongly correlated and exhibit properties that prefigure the long-range ordered behavior. At low temperatures, the spectra for 2–4 show distinct differences. For 2, a single resonance was observed down to base temperature. On the other hand, two resonances were observed in the low temperature spectra for 3 and 4, as indicated by the blue and red arrows in Figure 10b and c. It is known that ESR probes antiferromagnetic resonances when $T < T_N$ where the multiple resonances correspond to the applied field being parallel/perpendicular to the collective anisotropy field and/or different AFM modes in powder samples. In either case, the observation of multiple ESR transitions in the low temperature spectra for 3 and 4 reveals the presence of a collective anisotropy field in these two compounds. Due to the fact that no single-ion ZFS was found for 3 and 4 at high temperatures, the collective anisotropy fields are likely due to non-Heisenberg interactions between Ni(II) ions. By contrast, the anisotropy field in 2 is likely to be negligible as only a single transition is observed down to the lowest temperature.

Quantitative calculations of the anisotropy fields in 3 and 4 are complicated by the fact that the transition temperatures are significantly affected by the applied field (see the phase diagram in Figure 6). In the experimental temperature regime, most low temperature spectra spread across the phase boundary, which makes it very difficult to simulate the ESR spectra with any standard model. Qualitatively speaking, the spacing between the two resonances in 3 is almost 4 times of that of 4, suggesting the presence of a stronger anisotropy field in 3 than 4. This is confirmed by the spin-flop transition observed in the these two compounds (see below).

E. Pulsed Field Magnetization. Magnetization versus field data ($M$ vs $H$) were recorded between 0.45 and 10 K using pulsed-magnetic fields up to 60 T and are shown in Figure 11a. At low temperatures, all compounds exhibit a slow initial rise in $M$, which gradually increases in slope until the critical field ($H_c$) is approached. $\mu_dH_c = 6.9(6)$, 6.1(3), and 5.8(1) T for NiCl$_2$(pyz)$_2$ (1), NiBr$_2$(pyz)$_2$ (2), and Ni(NCS)$_2$(pyz)$_2$ (4), respectively, as defined by the midpoint between the peak in $dM/dH$ (indicated by * in the inset to Figure 11) and the region where $dM/dH$ remains essentially constant (inset to Figure 11). The slight concavity of the $M$ vs $H$ curve is expected for antiferromagnetic $S = 1$. In the case of NiCl$_2$(pyz)$_2$ (3), the $dM/dH$ curve exhibits extra steps between 6 and 10 T, which may be attributed to non-Heisenberg exchange interactions as well as the polycrystalline nature of the sample. The presence of non-Heisenberg interactions can give rise to an anisotropic critical
In the calculation, we neglected the interlayer interactions (eq 4). Inset: dH/dfield data (see section 4). For Ni(NCS)2(pyz)2 (black) employing an isofield for NiCl2(pyz)2 (red), Ni(I) (pyz)2 ( purple), and Ni(III) (pyz)2 (black) employing an S = 1 square lattice with interlayer interactions (eq 4). Inset: dH/dfield plot for the calculated magnetization. The dashed lines in both the main plot and the inset represent the simulation for NiBr2(pyz)2 including a broadening effect induced by g-strain.

field, leading to extra steps at high fields in the dH/dfield curve of a powder sample. The critical field for 3 is defined by the midpoint between the last kink in dH/dfield and the region where dH/dfield drops to zero. It is noteworthy that due to the possibility of an anisotropic critical field, this assigned value [9.4(1) T] for the low-field transition in the vicinity of Hc could be reproduced by an Ising-like interaction with Jx = 1.34 K for 3 and Jy = 0.42 K for 4. In the simulations, the ratio between Jxy and Jzz was fixed according to the magnetic dimensionality analysis (see section 4 and Table 3), while their values have been slightly fine-tuned to match the experimental data. Additionally, we allowed an Ising-like interaction with Jx = 1.35 and 1.20 for 3 and 4, respectively, to account for the low-field spin–field transition. As shown in Figure 11, good agreement between the experiments and simulations was obtained for 2 and 4. For 2, the rounded feature of M in the vicinity of Hc could be reproduced by

![Figure 11](https://example.com/figure11.png)

Figure 11. (a) Main plot: Isothermal magnetization for NiCl2(pyz)2 (red), NiBr2(pyz)2 (black), Ni(I) (pyz)2 ( purple), and Ni(III) (pyz)2 (black) employing an S = 1 square lattice with interlayer interactions (eq 4). Inset: dH/dfield plot showing the spin–field transition (Bc) and critical fields (Bc). (b) Main plot: Calculated magnetization M for NiBr2(pyz)2 (red), Ni(I) (pyz)2 ( purple), and Ni(III) (pyz)2 (black) employing an S = 1 square lattice with interlayer interactions (eq 4). Inset: dH/dfield plot for the calculated magnetization. The dashed lines in both the main plot and the inset represent the simulation for NiBr2(pyz)2 including a broadening effect induced by g-strain.

| Table 3. Magnetochemical Parameters Obtained for 1–4 |
|-------------------|------------------|-----------------|-----------------|
| Ipyr (K)          | Jz (K)           | D (K)           | g[χ(T)]         | g (ESR)         | Tnx (K)         | μ0Hc (T)        |
| NiCl2(pyz)2 1     | 0.49 ± 0.01      | < 0.05          | 8.03 ± 0.16     | 2.15 ± 0.05     | n/a             | 6.9 ± 0.6       |
| NiBr2(pyz)2 2     | 1.00 ± 0.05      | 0.26 ± 0.05     | 0               | 2.10 ± 0.09     | 2.20 ± 0.05     | 1.8 ± 0.1       |
| Ni(I) (pyz)2 3    | < 1.19           | > 1.19          | 0               | 2.41 ± 0.03     | 2.27 ± 0.08     | 2.5 ± 0.1       |
| Ni(III) (pyz)2 4  | 0.82 ± 0.05      | 0.47 ± 0.05     | 0               | 2.10 ± 0.04     | 2.16 ± 0.01     | 1.8 ± 0.1       |

“The Ipyr, D, and g for NiCl2(pyz)2 1 were obtained by fitting the DC susceptibility to an anisotropic 2D model, while its Jz was estimated based on the heat capacity data (see section 3B). The g values obtained via ESR data and through fitting of g[χ(T)] are both listed in the table for comparison. The parameters for NiBr2(pyz)2 2, Ni(I) (pyz)2 3, and Ni(III) (pyz)2 4 were determined by analysis of the heat capacity, ESR, and pulsed magnetic field data (see section 4).
including a disorder induced $g$ strain which leads to a Gaussian distribution of the $g$ factor. The inclusion of the Ising-like interactions ($\Delta > 1$) leads to a spin-flop transition in 3 and 4, as shown by the anomaly in $d\chi/dH$. However, the simulation for 3 does not show any obvious kink at high fields in $d\chi/dH$ with $\Delta$ alone. The Ising-like interactions in 3 give rise to a 0.2 T difference between the critical fields with $B \parallel z$ and $B \perp z$, which appears to be insufficient to explain the high-field feature in experiments, suggesting additional anisotropy terms are needed to explain the magnetization data for 3.

Further investigations are required to fully understand the spin-flop transition in 3 and 4. The anisotropic part of the interaction, $f(\Delta - 1)$, should be proportional to $(\Delta g/g)^2$, where $\Delta g$ is the $g$ anisotropy of Ni(II). Therefore, it seems to be contradictory to include an Ising-type interaction, whereas no $g$ anisotropy was observed in the ESR data. We suspect that the single-ion anisotropy of Ni(II) is not fully resolved due to non-Heisenberg interactions which broaden the ESR spectra. Further experiments have been proposed on their magnetically diluted congeners, Zn$_1$Ni$_{X_2}$(pyz)$_x$ alone. The Ising-like interactions in Figure 12. upon cooling from 300 K, $\chi(T)$ increases smoothly, reaching a broad maximum near 2.6, 2.4, 2.7, and 2.2 K for 1, 2, 3, and 4, respectively, and then drops slightly as the temperature is lowered to 2 K. This behavior can be caused by concomitant antiferromagnetic (AFM) coupling between $S = 1$ Ni(II) sites and/or ZFS of the spin ground state. Curie–Weiss fits of the reciprocal susceptibility in the temperature range of 50 $< T <$ 300 K lead to $g = 2.17(7)$ and $\Theta = -3.51(23)$ K (1), $g = 2.10(9)$ and $\Theta = -3.20(36)$ K (2), $g = 2.41(3)$ and $\Theta = -5.02(6)$ K (3), and $g = 2.10(4)$ and $\Theta = -4.00(23)$ K (4). In the absence of single-ion anisotropy, the negative Curie–Weiss temperatures would indicate the presence of AFM interactions in 1–4. The fitted $g$ values for 2 and 4 are in good agreement with the ESR results. The fitted $g$ value for 3 deviates from the ESR result ($g = 2.27$) and appears to be too large for Ni(II). It is well-known that the $g$ factor obtained from susceptibility can be affected by many experimental parameters, e.g., errors in the sample mass, whereas ESR gives a direct measurement for the $g$ factor. Therefore, for 2–4, the $g$ factors extrapolated from the ESR data were used in the following data analysis.

Based on the information obtained from the heat capacity and ESR studies, the $\chi(T)$ data for 2–4 were fitted to an $S = 1$ simple cubic Heisenberg model, $H = J \sum \langle S_i \cdot S_j \rangle$. This model assumes that (a) the intra-/interlayer interactions are the same ($J$), and (b) the number of nearest magnetic neighbors, $z$, is 6, both of which may be oversimplifications. As we will mention in the Discussion section, this model cannot account for the ordering temperature. Nevertheless, we can still use it to compare $z$ with the pulsed field magnetization data. Figure 12 shows the data and fits for 2–4 over the entire temperature range with the fitting parameters of $J = 0.82(5)$ K (2), $J = 1.00(4)$ K (3), and $J = 0.75(2)$ K (4). These interactions would predict critical fields of $\mu_0H_c = 6.66$, 8.4, and 6.2 T for 2, 3, and 4 ($g = 2.20$), $g = 2.27$ (3), and 2.16 (4) from the ESR data), respectively. The estimated critical fields for 2 and 4 are in excellent agreement with the pulsed field data. The estimated critical field for 3 is slightly less than that measured in the magnetization data. However, as we mentioned in the previous section, the possibility of an anisotropic $H_c$ may lead to an overestimation in the magnetization data, which could account for this difference.

The susceptibility for 1 was fitted employing an anisotropic 2D model (Figure 12a). The fit gives $z_{pyz} = 1.97(4)$ K, $D = 8.03(16)$ K, and $g = 2.15(5)$. Taking $z$ = 4 (for Q2D model), $J_{pyz} = 0.49(1)$ K, which is almost half of that in 2–4. The fitted easy-plane type anisotropy $D$ = 8.03 K gives rise to a broad peak (Schottky anomaly) around 3 K which coincides with the broad feature in C$_s$ for 1. However, extracting D and J simultaneously from powder magnetic data can often be unreliable as the two parameters are highly correlated. The result is not unique and varies dramatically depending on the model employed in the analysis. In fact, the susceptibility data for 1 can be fitted with an isolated $S = 1$ model with $D = 13.3$ K. However, this would predict a broad peak around 5 K in the zero-field heat capacity, which significantly deviates from the experimental results. Therefore, both $D$ and $J$ are required for characterizing 1. Because single crystals for 1 are currently unavailable, it is not possible to distinguish between the parallel and perpendicular susceptibilities in order to uniquely determine the sign and magnitude of $D$.

As an additional evaluation of the magnetic interactions, density functional theory (DFT) calculations were performed using the aforementioned structural data for 1–4. The magnetic interactions through the pyz bridges were modeled by the dinuclear fragments, (pyz)$_2$NiX$_x$(pyz)$_y$, consisting of two (pyz)$_2$NiX$_x$ segments connected by a bridging pyz ligand ($\mu$-pyz), which mediates the intralayer interaction $J_{pyz}$. The calculations give weak AFM interactions mediated by Ni–pyz–Ni bonds throughout all compounds as expected. $J_{pyz}$ is calculated to be 1.85, 2.41, and 3.16 K for compounds 1, 2, and 3, respectively. Separate DFT calculations were performed for 4 due to its lower symmetry (C$_2$/m vs I4/mmm for 1–3). In general, the adjoining orthogonal pyz bridges in 4 afford different magnetic interactions depending on whether the Ni–Ni linkage lies in or perpendicular to the Ni–NCS planes. Therefore, DFT
calculations for 4 were performed with both configurations to investigate the influence of the NCS ligand orientation on $J_{pyz}$. A small difference in $J_{pyz}$ was found for these two configurations with $J_{pyz}$ calculated to be 1.65 and 1.71 K for the Ni–Ni axis in and perpendicular to the Ni–NCS planes, respectively. The calculation for 4 suggests that $J_{pyz}$ is almost independent of the orientation of the NCS ligands; hence, it is reasonable to treat the [Ni(pyz)$_2$]$^{2+}$ layers in 4 as ideal magnetic square lattices in the data analysis.

4. DISCUSSION

Each of the four compounds share similar extended polymeric structures consisting of 2D square [Ni(pyz)$_2$]$^{2+}$ sheets in the $ab$ plane with the $X$ ligands acting as spacers between layers. The Ni–Ni separations are similar along the Ni–pyz–Ni bridges. There is little variation of the closest interlayer Ni–Ni distance across all four compounds (7.32 Å for NiCl$_2$(pyz)$_2$ (1), 7.54 Å for NiBr$_2$(pyz)$_2$ (2), 7.90 Å for NiI$_2$(pyz)$_2$ (3), and 7.23 Å for Ni(NCS)$_2$(pyz)$_2$ (4)). The difference in the magnetism of 1–4 clearly highlights that the selection of the $X$ ligand can lead to significant changes in both the single-ion anisotropy and the magnetic dimensionality in this NiX$_2$(pyz)$_2$ family.

Thorough investigations have been performed to quantify the magnetic interaction through $X$-bridges in CuX$_2$(pyz) compounds ($X = F, Cl, Br$ and NCS). For CuX$_2$(pyz) compounds possess 2D rectangular lattices which are characterized by Cu–pyz–Cu chains linked by Cu–X–Cu bridges. We briefly review the interactions through the Cu–X–Cu bridges since they are likely related to the interlayer interactions through the $X$ ligands in compounds 1–4. In CuX$_2$(pyz) compounds, the AFM interactions through Cu–X–Cu bonds were found in the descending order of magnitude: Br $>$ Cl $>$ F $>$ NCS. In particular, Cu(NCS)$_2$(pyz) presents itself as a nearly ideal Q1D AFM chain with the primary 1D interactions mediated through the Cu–pyz–Cu bridges. μSR measurements for Cu(NCS)$_2$(pyz) show no evidence for LRO above 0.35 K, which is indicative of extremely weak interchain interactions ($<0.13$ K) through the Cu–NCS–Cu bonds. Therefore, it is at first glance surprising to see that Ni(NCS)$_2$(pyz)$_2$ (4) shows a strong λ-anomaly as the interlayer interactions via the NCS$^-$ ligands are expected to be small. On the other hand, the difference between NiCl$_2$(pyz)$_2$ (1) and NiBr$_2$(pyz)$_2$ (2) may be explained by the previous studies with the less efficient Cl pathways leading to Q2D magnetism in 1. The results for NiI$_2$(pyz)$_2$ (3) are in line with this hypothesis that the larger I$^-$ ions can form more effective exchange pathways between [Ni(pyz)$_2$]$^{2+}$ layers, leading to stronger interlayer interactions. Consequently, a larger λ-anomaly and a higher $B_c$ are observed in the $C_p$ and the magnetization data.

A similar λ-anomaly in $C_p$ was observed in a compound isomorphous to 4, Fe(NCS)$_2$(pyz)$_2$, which is regarded as an Ising Q2D antiferromagnet. Although Q2D order is achieved below 6.8 K, its critical parameters are ideally close to those expected for Q2D Ising systems. In the case of 2, the scenario for an Ising Q2D antiferromagnet is excluded due to the facts that (a) the ZFS of the Ni(II) ions in 2 is found to be negligible and (b) both the ESR and magnetization data show no evidence of a collective anisotropie field at low temperatures. For 3 and 4, the absence of single-ion anisotropy in their paramagnetic phase is also unfavorable of extreme Ising Q2D antiferromagnets. In particular, the phase boundary of 4 is similar to that of 3D antiferromagnets, providing additional support for 3D antiferromagnetism in 4. Therefore, it is most likely that the $X$ ligands serve as bridging ligands in 2–4, which mediate interlayer interactions that are comparable to the intralayer interactions, leading to AFM long-range order. The difference between the NCS$^-$ bridges in Cu(NCS)$_2$(pyz) and 4 remain to be examined. The shortest Ni–S distance in 4 is 4.719 Å, which is unlikely to form a direct Ni–S exchange pathway. Therefore, the interlayer interactions in 4 may be mediated through overlapping electron density among NCS$^-$ ligands connected to Ni(II) ions belonging to adjacent layers.

In discussing the susceptibility for 1–4, a simple cubic model was employed for the data analysis. However, the legitimacy of using such a model needs to be justified. It is clear that each Ni(II) ion has four magnetic neighbors in its [Ni(pyz)$_2$]$^{2+}$ plane for all four compounds. However, it is not straightforward to tell the number of magnetic neighbors in the adjacent planes from the crystal structures. For 1–3, each Ni(II) ion has eight equally spaced neighbors in the adjacent planes. In the case of perfect tetragonal symmetry, this gives eight equivalent magnetic neighbors in the adjacent planes for a Ni(II) site, leading to frustration of the minimum-energy configuration if the interactions within the [Ni(pyz)$_2$]$^{2+}$ planes are antiferromagnetic. In this case, 1–3 would only show two-dimensional order within the [Ni(pyz)$_2$]$^{2+}$ planes, and the λ-anomaly would be significantly suppressed, contrary to the experimental observations. Therefore, we speculate that the frustration is relieved via breaking of the tetragonal symmetry, possibly due to the structural disorder of the pyz rings, resulting in 3D LRO in 2 and 3. A reduced symmetry should give rise to four inequivalent interlayer interactions in 1–3 with one of them being stronger than the others. Compound 4 crystallizes in a monoclinic space group where one would expect four inequivalent interlayer interactions based on its structure. Therefore, it is reasonable to assume that the interlayer interactions are dominated by one particular pathway in 1–4, and each Ni(II) ion has two magnetic neighbors in the adjacent planes (one in the plane above/below). Although this is probably an oversimplification, it is the simplest model one can adopt is consistent with the experimental results.

The critical fields measured in the pulsed magnetic field data provide a reliable way to probe the interactions between Ni(II). Here, we focus on 2–4, for which no single-ion ZFS was observed by ESR. Consequently, $B_c = \mu_B H$, solely depends on the intra- and interlayer interactions. The critical field for 1 depends on both $D$ and $J$, and it is not possible to deconvolute them from pulsed field data alone. For quantitative calculation of the intra- and interlayer interactions, the critical fields and the Néel temperatures for 2–4 are analyzed within a Q2D Heisenberg model. For $S = 1$ Q2D Heisenberg antiferromagnets, the critical field is

$$\mu_B g R = 8 J_{pyz} + 4 J_L$$

where $J_L$ is the interlayer interaction. Yasuda et al. proposed an empirical correlation between $T_N$ and the interactions based on quantum Monte Carlo calculations for $S = 1$ Q2D Heisenberg antiferromagnets:

$$T_N = 4\pi \times 0.68 J_{pyz} + [3.12 - \ln(J_L/J_{pyz})]$$

Equation 6 is valid in the range $0.001 \leq J_L/J_{pyz} \leq 1$. In the analysis, we assumed $\Delta = 1$ due to the lack of theoretical study to correlate $\Delta$ and $T_N$ in $S = 1$ antiferromagnets. Applying eq 5 and eq 6 to 2–4, it is found that the experimental results for 2 and 4 can be accounted for with the following parameter sets: $J_{pyz} = 1.0$ and $J_L = 0.26$ K for 2 and $J_{pyz} = 0.82$ and $J_L = 0.47$ K for 4.
The obtained \(I_{pyz}\)'s are similar for 2 and 4, which is consistent with the structural similarities between their \([Ni(pyz)_{2}]^{2+}\) layers. \(J_{x}/J_{pyz} = 0.26\) and 0.57 for 2 and 4, respectively, indicating 2 is a 3D antiferromagnet which prefigures some Q2D magnetism, whereas 4 is more similar to an ideal 3D antiferromagnet in which the intra- and interlayer interactions are equivalent. The difference in \(J_x/J_{pyz}\) explains the reduction of the \(\lambda\)-anomaly in 2. On the other hand, no \(J_x\) and \(J_{pyz}\) can satisfy eq 5 and eq 6 simultaneously for 3, suggesting it does not fall into the category of a Q2D antiferromagnet. We suspect that the large \(\Gamma\) ligands form efficient exchange pathways which propagate strong interlayer interactions, leading to \(J_x > J_{pyz}\) in 3. Hence, its LRO temperature and critical field cannot be interpreted in terms of a Q2D antiferromagnet. Absence of an adequate theoretical model for an \(S = 1\) antiferromagnet with \(J_x > J_{pyz}\) it is difficult to calculate \(J_x\) and \(J_{pyz}\) independently. In the case of an ideal 3D antiferromagnet, \(J_x = J_{pyz} = 1.19\) K for 3. With \(J_x > J_{pyz}\) eq 5 suggests \(J_{pyz} < 1.19\) K for 3. However, among the four compounds, 3 exhibits the strongest \(\lambda\) anomaly, indicating that it is reasonably close to a 3D antiferromagnet. Accordingly, we expect \(J_{pyz}\) for 3 to be in the vicinity of 1 K. The resulting parameters for 1–4 are summarized in Table 3.

Finally, we compare the results of 1–4 with those of \([Ni(HF_2)(pyz)_{2}]Z\) (\(Z = PF_{6}^{-}\) and \(SbF_6^{-}\)). The 2D \([Ni(pyz)_{2}]^{2+}\) layers found in 1–4 exhibit very similar geometrical parameters to those of \([Ni(HF_2)(pyz)_{2}]Z\). The \([Ni(HF_2)(pyz)_{2}]Z\) compounds were found to be quasi-1D magnets composed of \(Ni–HF–Ni\) chains (\(J_{1d}\)) with interchain coupling (\(J_{1c}\)) mediated by \(Ni–pyz–Ni\) linkages. The interaction parameters were not determined due to difficulties in distinguishing between \(J_{1d}/J_{1c}\) and \(D\) from pulsed field data as above. The couplings through \(Ni–pyz–Ni\) bridges in 2–4 are found in the vicinity of 1 K, which are significantly smaller than \(J_{1d}\) determined for \([Ni(HF_2)(pyz)_{2}]Z\). Such results are consistent with the Q1D magnetism of \([Ni(HF_2)(pyz)_{2}]Z\). Our study also shows that the effect of the axial \(X\) ligands can substantially vary the ZFS of the \(Ni(II)\) ion as well as potentially introduce non-Heisenberg interactions between \(Ni(II)\) ions, leading to different magnetic ground state structures in \(Ni(II)\)-based magnets.

5. SUMMARY

Four \(Ni(II)\)-based coordination polymers were prepared and their structures carefully examined. \(NiCl_2(pyz)_{2}\) (1), \(NiBr_2(pyz)_{2}\) (2), \(NiI_2(pyz)_{2}\) (3), and \(Ni(NCS)_2(pyz)_{2}\) (4) feature 2D square \([Ni(pyz)_{2}]^{2+}\) planes stacking along the \(c\) axis spaced by \(X\) ligands (\(X = Cl, Br, I,\) or \(NCS\)). Heat capacity measurements are indicative of the presence of long-range order for 2–4 and Q2D magnetism for 1. The \(\mu SR\) data for 1 suggest that a transition occurs at 1.5 K. The single-ion magnetic properties of 2–4 were measured by ESR where no evidence of ZFS was found. Pulsed-field magnetization data show that the critical fields for 1–4 vary from 5.8 to 9.4 T, which are significantly smaller than those for \([Ni(HF_2)(pyz)_{2}]Z\) (\(Z = PF_{6}^{-}\) and \(SbF_6^{-}\)). Taken together, the magnetic property measurements reveal the interlayer interaction can be suppressed by the choice of the \(X\) ligand. Despite the differences in the interlayer interactions, the \(Ni–pyz–Ni\) interactions in 2–4 remain largely unaltered and are found to be in the vicinity of 1 K. This result is in keeping with the prominent \(\lambda\)-anomaly in the heat capacity data, and excellent agreement for \(T_C\) was achieved between experiment and QMC predictions for 2 and 4. The obtained \(I_{pyz}\) values are consistent with the Q1D magnetism found in the \([Ni(HF_2)(pyz)_{2}]Z\) family. Compound 1 possesses a finite ZFS and reduced magnetic dimensionality.

This study, in combining with the previous work on the \([Ni(HF_2)(pyz)_{2}]Z\) family, reveals that prudent ligand choice may allow systematic tuning of the interlayer interaction between \([Ni(pyz)_{2}]^{2+}\) planes, permitting the preselection of Q1D, Q2D, and 3D magnetism.

In addition to controlling the magnetic dimensionality, lattice randomness in low-dimensional \(S = 1\) antiferromagnets can lead to a highly nontrivial phase diagram.8 Such randomness can be introduced in molecule-based magnets by doping the system with diamagnetic ions, e.g., \(Zn(II)\), and the concentration of dopants can be controlled in the synthesis. The compounds studied in this work offer a promising opportunity for studying the effect of lattice randomness and other cooperative phenomena.

Improvements in the experimental testing of low-dimensional \(S = 1\) antiferromagnets require better models for understanding the physics. Specifically, a model to calculate the ordering temperature considering both the influence of the ZFS parameter \(D\) and the exchange anisotropy is strongly desired for interpreting experimental data. In addition, further DFT studies are required for a better appreciation of the mechanisms of the magnetic interactions as well as the ZFS of \(Ni(II)\) ions. Such studies can allow prediction of magnetic properties based on crystaline architectures. The possibility to target molecule-based magnets as effective simulators of low-dimensional magnetism is ensured by a crystal engineering approach as was demonstrated in this work. Future work on 1–4 will entail detailed neutron scattering studies.

ASSOCIATED CONTENT

5. Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b02991.

Figure S1, synchrotron X-ray powder diffraction pattern and Rietveld fit for \(NiCl_2(pyz)_{2}\) (1); Figure S2, synchrotron X-ray powder diffraction pattern and Rietveld fit for \(NiBr_2(pyz)_{2}\) (2); Figure S3, synchrotron X-ray powder diffraction pattern and Rietveld fit for \(NiI_2(pyz)_{2}\) (3); Figure S4, synchrotron X-ray powder diffraction pattern and Rietveld fit for \(Ni(NCS)_2(pyz)_{2}\) (4); and Figure S5, comparison of X-ray powder patterns for \(NiCl_2(pyz)_{2}\) assuming \(I4/mmm\) and \(Ccc\) space group symmetries (PDF).

Crystallographic information for compound 1 (CIF)
Crystallographic information for compound 2 (CIF)
Crystallographic information for compound 3 (CIF)
Crystallographic information for compound 4 (CIF)

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Notes

The authors declare no competing financial interest.

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