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Enhancing easy-plane anisotropy in bespoke Ni(II) quantum magnets

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A B S T R A C T
We examine the crystal structures and magnetic properties of several $S=1$ Ni(II) coordination compounds, molecules and polymers, that include the bridging ligands HF$_2$, AF$_4$ (A = Ti, Zr) and pyrazine or non-bridging ligands F, SiF$_6$, glycine, H$_2$O, 1-vinylimidazole, 4-methylpyrazole and 3-hydroxypyridine. Pseudo-octahedral Ni$_x$F$_y$, Ni$_x$O$_y$ or Ni$_x$OF cores consist of equatorial Ni-N bonds that are equal or non-bridging ligands F

1. Introduction

Low-dimensional magnetism continues to be of great interest to the chemistry and physics communities [1–5]. To a large extent, the resurgence of this field may be attributed to the award of the 2016 Nobel Prize in Physics to Kosterlitz and Thouless for their theoretical work on the XY model (also known as easy-plane or planar – i.e., systems exhibiting circular symmetry [6]) and to Haldane for his efforts to realize topological states in integer-spin systems [7]. We are interested in the experimental realization and characterization of these models and how they impact the bulk properties of molecule-based $S=1$ quantum magnets. In this context, a crucial parameter to be evaluated and, possibly predicted, is the zero-field splitting (ZFS) as it determines the magnetic ground-state of a compound was found to be easy-plane ($D>0$) and range from $\approx 8$–25 K. This work reveals a linear correlation between the ratio $d/(Ni_{eq}-L_{ax})$ and D although the ligand spectrochemical properties may play an important role. We assert that this relationship allows us to predict the type of magnetocrystalline anisotropy in tailored Ni(II) quantum magnets.

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ligand-field [9]. A combination of experimental probes is generally required to untangle D from the exchange interactions (J) as they tend to be highly correlated when considering bulk data. Thermodynamic measurements such as heat capacity (C_v), high-field magnetization (M), magnetic susceptibility (χ) and inelastic neutron scattering (INS) can be used to assess the ZFS but caution is warranted in the analysis and interpretation of such data obtained for powder samples [10].

If the dominant intrachain/intralayer J is weak relative to D and a field/frequency combination is able to access the relevant excitations, electron-spin resonance (ESR) [11] is the preferred probe for measuring the axial D and rhombic E-terms in the Heisenberg spin Hamiltonian (Eq. (1)).

\[
\hat{H} = J \sum_{i<j} \hat{S}_i \cdot \hat{S}_j + J' \sum_{i\neq j} \hat{S}_i \cdot \hat{S}_j + D \sum_i \left( \hat{S}_i^2 \right)^2 + E \sum_i \left( \hat{S}_i^2 - \hat{S}_i^z \right)^2 + \mu_B \sum_i B \cdot \hat{S}_i \quad (1)
\]

In this expression, \( \hat{S} \) is the spin operator of each ion \( i \), \( i,j \) denotes the sum over unique nearest-neighbors, \( J \) is due to intrachain/layer interactions and the isotropic Landé g-factor defines the Zeeman energy. Positive \( J \) and \( J' \) values denote antiferromagnetic (AFM) interactions. For an exchange-free system, the first two terms of the Hamiltonian are negated leaving only the single-ion anisotropy parameters to be determined. The sign of \( D \) establishes the preferred orientation of the magnetic moments in a paramagnetic material; i.e. \( D > 0 \) (XY) and \( D < 0 \) (Ising; also known as axial or easy-axis). The energy-scale of \( D \) can be such that its effects persist well above \( T_N \) and compete with thermal fluctuations. For \( S = 1 \) and the scenario \( D > 0 \), the ground state is a singlet \( (m_s = 0) \) and lies below the \( m_s = \pm 1 \) doublet. This means that the Ni(II) magnetic moments prefer a planar orientation perpendicular to the unique axis.

Knowledge of \( D \) and its size in proportion to exchange interactions allows a material to be placed on the appropriate phase diagram including, but not limited to, the quasi-1D AFM chain [12]. Unique combinations of these parameters (as well as ancillary couplings \( J \)) may lead to new quantum states and theories, as well as permitting access to quantum critical points (QCP) [13].

Molecular materials are particularly well suited for such studies, as the ligand-field and metal-metal spacings may be synthetically manipulated, permitting D and J to be tuned [14]. To this end, we are examining magnetostructural correlations in low-dimensional \( (\text{zero-}, 1- \text{and 2D}) \) systems that contain trans-coordinated ligands \( \text{L} \) situated in pseudo-octahedral \( \text{NiF}_2 \), \( \text{NiO}_2 \) or \( \text{NiO}_6 \) environments. Equatorial sites consist of \( \text{N-donor atoms} \) that belong to pyrazine (pyz), glycine (gly), 1-vininimidazole (vinim), 4-methylpyrazole (mezp) or 3-hydroxypryidine (OHpy). Systematically, it was found that these materials display easy-plane magnetic anisotropy regardless of the structural dimensionality or presence of mild distortion \( (E \neq 0) \) around the Ni(II) center [15]. For some of these systems, \( D \) and \( J \) are similar in scale and, in others, \( D \gg J \). Herein, we examine these \( D-J \) combinations by analyses of X-ray crystal structures and magnetic properties of targeted Ni(II) compounds, molecular and polymeric. We discovered that the experimental D-values linearly track \( d(\text{Ni}-\text{Lax})/d(\text{Ni}-\text{Nax}) \) and that this correlation also depends upon the spectrochemical properties of the axial \( \text{L} \), which are \( F^- \), \( \text{HF}_2^- \), \( \text{AF}_6^- \) \( (A = \text{Si, Ti, Zr}) \) or oxygen \( (\text{from gly or H}_2\text{O}) \). Relative to the stronger field amine ligands, stark differences in ligand-field strength and donor-atom electronegativity of \( L_{ax} \) leads to \( D \)-values up to 25 K. Taken together, this work establishes a predictive strategy to design Ni(II) quantum magnets with \( D > 0 \).

2. Experimental section

2.1. Syntheses

All chemicals were purchased from commercial suppliers and used without further purification. CAUTION! Fluorinated acids, including 48–51% aqueous hydrofluoric acid, are extremely dangerous and must be handled with great care. Appropriate personal protective equipment must be worn even if handling small quantities.

\[\text{[Ni(HF}_2\text{)(pyz)]SbF}_6\] (1). As reported in detail elsewhere, aqueous-HF solutions of \( \text{NiF}_2 \cdot 4\text{H}_2\text{O}, \text{NH}_4\text{HF}_2 \), NaSbF_6 and pyz were slowly mixed to produce a green solution that was covered with perforated Parafilm\textsuperscript{m} [16]. Upon standing at room temperature for ~12 h, a blue micro-crystalline solid began to form on the walls and bottom of the plastic beaker. At this point, the beaker was tightly sealed with a fresh sheet of unperforated Parafilm\textsuperscript{m} and left to stand in a fumehood. After about one year, the solution completely evaporated leaving a large mass of small blue crystals and a few conglomerates of colorless crystals assumed to be \( \text{NH}_4\text{F} \). The blue crystals were initially characterized by IR spectroscopy followed by laboratory-based single crystal X-ray diffraction which confirmed the material to be 1. The extremely slow solvent evaporation proved imperative in producing crystals of suitable size for the X-ray study.

\[\text{NiF}_2\text{(pyz)}_2 \cdot 3\text{H}_2\text{O} \] (2). \( \text{NiF}_2 \cdot 4\text{H}_2\text{O} (0.3503 \text{ g}, 2.07 \text{ mmol}) \) was dissolved in 2-mL of aqueous HF (48–51% by volume) and slowly poured into a 10-mL aqueous solution containing a large excess of pyz (3.3157 g, 41.40 mmol). A blue solution formed immediately with no precipitate. The reaction mixture was stirred for an additional 30 min, covered with perforated Parafilm\textsuperscript{m} and left to stand at room temperature in the fumehood. After one-day, a small amount of pale blue precipitate was observed. Upon standing for another 7 days, the precipitate became darker blue with much more material forming on the walls and bottom of the plastic beaker. The solid was scraped off of the beaker, filtered using vacuum filtration and washed with 10-mL of fresh \( \text{H}_2\text{O} \). As a final wash, 10-mL of \( \text{EtOH} \) and 20-mL of \( \text{Et}_2\text{O} \) were used successively to assist in drying the sample. The obtained product had a mass of 0.3643 g (57% yield) and was pale blue-gray in color.

\[\text{Ni(gly)}_2\text{(pyz)}_2 \cdot 5.2\text{H}_2\text{O} \] (3). While stirring, neat glycine (0.6324 g, 8.40 mmol) was added to a 20-mL hot aqueous suspension of \( \text{NiCO}_3 \) (0.5010 g, 4.21 mmol). To this teal colored solution was added neat pyrazine (0.3364 g, 4.20 mmol). Upon slow solvent evaporation overnight, a large mass of light brown needles formed on the walls and bottom of the beaker. The crystals were collected by vacuum filtration and lightly dried. Upon careful inspection a few small blue crystals, identified by X-ray diffraction as \( \text{Ni(gly)}_2(\text{H}_2\text{O})_2 \) [17], were found and mechanically separated. The total collected mass of product was 0.9089 g (57% yield) based on Ni ion.

\[\text{Ni(AF}_6\text{)(vinim)}_4 \] (A = Ti, 4a and 4b; A = Zr, 5). \( \text{Ni(NO}_3\text{)}_2 \cdot 6\text{H}_2\text{O} (0.2004 \text{ g}, 0.69 \text{ mmol}) \) was dissolved in 3-mL of \( \text{H}_2\text{O} \) and mixed with a 5-mL aqueous solution containing (\( \text{NH}_3\text{)}_2\text{TiF}_6 \) (0.1682 g, 0.85 mmol) and vinim (0.2861 g, 3.04 mmol). While stirring, a pale blue precipitate (4a) formed immediately which was collected by vacuum filtration, washed with 2-mL \( \text{H}_2\text{O} \), followed by 2-mL \( \text{EtOH} \) and dried in vacuo. Small blue-purple prisms (4b) suitable for X-ray diffraction were grown by slow evaporation of dilute 1:1 aqueous \( \text{EtOH} \) solutions. \( \text{Ni(ZrF}_6\text{(vinim)}_4 \) (5) was synthesized in a similar manner but replacing (\( \text{NH}_3\text{)}_2\text{TiF}_6 \), (\( \text{NH}_3\text{)}_2\text{ZrF}_6 \). Typical product yields of 4a, 4b and 5 were 25–35% based on vinim.

\[\text{Ni(SiF}_6\text{(mezp)}_2 \cdot (\text{H}_2\text{O}) \cdot 2\text{H}_2\text{O} \] (6). \( \text{NiF}_2 \cdot 6\text{H}_2\text{O} (0.4500 \text{ g}, 1.46 \text{ mmol}) \) was dissolved in 2-mL of water and added dropwise to a 20-mL \( \text{EtOH} \) solution containing 4-methylpyrazole (0.4795 g, 5.64 mmol) to produce a teal colored solution. The reaction mix-
ture was covered with Al-foil and left to stand undisturbed at room temperature. After about 2 hrs, a green precipitate formed which was removed by vacuum filtration. The mother liquor remained teal in color and was again set aside to slowly evaporate. Upon standing for approximately 18 h, a large mass of deep blue crystals formed. These were collected by vacuum filtration and gently air-dried for about 30 min. The crystalline product was obtained in 54% yield (0.4434 g) based on meq.

NiF$_2$(OHpy)$_4$(7). A 10-ml aqueous solution containing dissolved Ni(NO$_3$)$_2$·6H$_2$O (0.2010 g, 0.69 mmol) was slowly added to a 40-ml 50:50 H$_2$O/EtOH solution containing NH$_4$HF$_2$ (0.0981 g, 1.72 mmol) and four equivalents of 3-hydroxypyridine (0.2653 g, 2.76 mmol). A pale green solution formed immediately without any precipitate. The beaker was covered with perforated Al-foil and left to stand at room temperature. After several minutes, a grey-green precipitate began to form. The reaction was allowed to continue overnight and the solid collected by suction filtration. Aliquots of 2-ml H$_2$O were used to wash the solid which was then dried in vacuo for 3 h. The material was obtained in 72% yield (0.2370 g) based on Ni(II) content. Crystals suitable for the X-ray diffraction study were recovered from the final product.

2.3. Synchrotron X-ray powder diffraction

High-resolution data were collected using beamline I11 located at the Diamond Light Source Ltd, Didcot, UK [22] and beamline 11-BM at the Advanced Photon Source, Argonne National Laboratory [23]. Samples of 2 (11-BM) and 4a (111) were prepared in 0.5-mm Kapton or borosilicate capillaries, respectively, and measured in transmission geometry. I11 used a position sensitive Mythen detector while discrete detectors were scanned over a 34° range in 2θ with data points collected every 0.001° on 11-BM. Data for 2 were collected only at room temperature whereas 4a was cooled to 100 K using a LN2 cryostream. Structural refinements were carried out using FULLPROF [24].

2.4. SQUID magnetometry

Linear susceptibility (χ = M/H) measurements were made for temperatures in the range 1.9 ≤ T ≤ 300 K and fields up to 7 T using a Quantum Design Magnetic Property Measurement System (MPMS) equipped with a standard dc transport. Powder samples with masses of 2–5 mg were packed in gelatin capsules, loaded in a plastic drinking straw, affixed to the end of a stainless steel/brass rod, and mounted on the transport. Samples were cooled in zero magnetic field to 1.9 K, the field charged to 0.1 T and data taken upon warming.

2.5. Pulsed-field magnetization

Measurements on each sample were made up to 60 T using a 1.5 mm bore, 1.5 mm long, 1500-turn compensated-coil susceptometer constructed from a 50 gauge high-purity copper wire [25]. When the sample is within the coil, the signal voltage V is proportional to dM/dt, where t is time. Numerical integration of V is used to evaluate M. The sample is mounted within a 1.3 mm diameter

<table>
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<th>3</th>
<th>4</th>
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<th>6</th>
<th>7</th>
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<td>Ni$_2$(F$_2$)(OHpy)$_4$</td>
<td>Ni$_2$(F$_2$)(OHpy)$_4$</td>
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<tr>
<td>Δρ = j$^*$ (e Å$^{-3}$)</td>
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<td>-0.727, 1.292</td>
<td>-0.218, 0.254</td>
<td>-0.389, 0.297</td>
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ampoule that can be moved in and out of the coil. Accurate values of $M$ were obtained by subtracting empty-coil data from that measured under identical conditions with the sample present. The susceptometer was placed inside a $^3$He cryostat providing a base temperature of 0.5 K. The magnetic field was measured by integrating $V$ induced in a 10-turn coil calibrated by observing the de Haas-van Alphen oscillations of the belly orbits of the copper wires in the susceptometer coil [25].

2.6. Electron-spin resonance

High-field, high-frequency ESR spectra of powdered samples at temperatures ranging from ≈ 3 to 20 K were recorded on a home-built spectrometer at the EMR facility of the National High Magnetic Field Laboratory using microwave frequencies 52–626 GHz. The instrument is a transmission-type device and uses no resonant cavity. The microwaves were generated by a phase-locked Virginia Diodes source, generating frequency of 13 ± 1 GHz, and equipped with a cascade of frequency multipliers to generate higher harmonics. A superconducting magnet (Oxford Instruments) capable of reaching a field of 17 T was employed.

2.7. Muon-spin relaxation

Zero-field muon-spin relaxation ($\mu$SR) studies [26] were carried out on a powder sample of 2 using the General Purpose Surface-Muon (GPS) spectrometer located at the Swiss Muon Source (SIS), Paul Scherrer Institute, Switzerland. The sample was wrapped in 25-μm Ag foil and mounted on a Cu fork using aluminized Mylar tape. Sample cooling was achieved using a side-loading continuous-flow $^4$He cryostat.

2.8. Electronic structure calculations

Computational modeling was executed on dinuclear moieties using the structural data from X-ray determinations. Evaluation of the exchange couplings was based on the broken-symmetry (BS) approach of Noodleman [27] as implemented in the ORCA version 4.1.1. suite of programs [28,29]. The formalism of Yamaguchi, which employs calculated expectation values $\langle S^2 \rangle$ for both high-spin and broken-symmetry states was used [30]. Auxiliary fitting bases were generated with the AutoAux procedure of ORCA [31]. Calculations related to magnetic interactions were performed using the PBE0 functional. The scalar relativistically reconstructed version of the Aldrichs triple-ζ basis set, def2-TZVP, was used for all atoms [32]. Numerical integrations for all DFT calculations were implemented using dense grids.

The ZFS were modeled by a complete active space self-consistent-field (CASSCF) approach employing the scalar relativistically contracted basis sets tailored for use with the Douglas-Kroll-Hess (DKH) Hamiltonian. The basis sets were of triple-ζ quality for all atoms (DKH-def2-TZVP) except for Zr where DKH-TZVP was employed within ORCA. In all calculations, the second order DKH Hamiltonian was used. For all systems, minimalistic, monomeric models based on the experimental geometries were used and the active space limited to the Ni d-orbitals.

3. Results and discussion

3.1. Structural and magnetic properties of a model $S = 1$ XY system [Ni(HF$_2$)(pyz)$_2$]SbF$_6$ (1)

Our interest in 1 was motivated by the desire to quantify two key parameters: (i) the exchange coupling ($J$) along the strong hydrogen bonded Ni-FHF-Ni pathway and (ii) the potentially large $D$ of the Ni(II) ion involved in Ni$_2$F$_2$ coordination. Initial difficulty in growing suitable single crystals limited experiments to powders and relied on high-magnetic field and neutron scattering techniques to untangle the $D$ and $J$ values [33]. A 3D XY magnetic ground-state was revealed wherein $D$ and $J$ are quantitatively similar. Using 1 as a prototype, we briefly review its magnetic properties to give context to the current work. Herein, new theoretical results on 1 are presented as well as the X-ray crystal structures and magnetic properties of several new molecule-based Ni(II) systems that also display large easy-plane anisotropy (see Table 3).

Table 2: X-ray structural and refinement parameters for Ni(TiF$_6$)(vinim)$_4$ (4a and 4b) and Ni(2TiF$_6$)(vinim)$_4$ (5).

<table>
<thead>
<tr>
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$\Delta E = 2\pi \hbar J / k_B T = S(S + 1)[1 + 2\sin \theta / R_{tot}]^{-1}$, where $R_{tot}$ is the average distance to the first nearest-neighbor chain. Structures and magnetic properties of several new molecule-based Ni(II) systems that also display large easy-plane anisotropy (see Table 3).

3.1.1. Crystal structure at 100 K [Ni(HF$_2$)(pyz)$_2$]SbF$_6$ (1) crystallizes in the tetragonal space group P4/mmm (S. G. #129) with Z = 2. Nearly isotropic NiF$_2$ octahedra (Fig. 1a) consist of two axially-ligated F-atoms belonging to HF$_2$ ions ([F$_2$]Ni-F1 = 2.074(2) Å) while the equatorial plane contains four pyz ligands coordinated through N-donor atoms ([F$_2$]Ni-N1 = 2.101(2) Å). The Ni(II) center lies on a 42/m site leading to a propeller-like disposition of the pyz rings which make a dihedral angle of 72.9(1)$^\circ$ with respect-to the ab-plane. A 3D MOF-like framework of composition [Ni(HF$_2$)(pyz)$_2$]$^+$ is formed owing to the bridging nature of the HF$_2$ and pyz ligands (Fig. 1b). Linear 1D Ni–HF–Ni Ni chains propagating along the c-axis with d (Ni–Ni) separations of 6.4292(3) Å. These chains are cross-connected by pyz ligands to afford [Ni(pyz)$_2$]$_{2n}$ square sheets with d (Ni–Ni) = 6.9965(4) Å. Thus, each Ni–HF–Ni chain is equidistant to four identical nearest-neighboring chains (n = 4). Voids within the framework are occupied by SbF$_6$ counterions.

From Fig. 1b it can be seen that two distinct types of hydrogen bonds exist; those internal to the HF$_2$–FHF–HF$_2$ anions via weaker C$\equiv$H–A–F interactions ([F$_2$]Ni–F1 = 2.490(2) Å; C$\equiv$H–F = 147.1(2)$^\circ$). We suggest that the latter H–B type restricts positional disorder of the pyz rings common to other tetragonal systems such as Ni(pyz)$_2$ (X = Cl, Br, I, NCO) [34,35]. The X = F material (see below) has monoclinic symmetry and does not exhibit pyz ring disorder.
3.1.2. Previously reported magnetic properties [33]

High-field $M(H)$ data were measured up to 60 T for a powder sample at several temperatures above and below $T_N = 12.2$ K, the latter being established by $C_p(T)$ and neutron diffraction. A slightly concave $M(H)$ curve and broad approach to saturation were observed (Fig. 2a), signifying low-dimensional AFM spin correlations and the presence of a large $D$-value, respectively. Within the easy-plane model, $g_{\text{eff}}\mu_BH_{\text{sat}} = 25\langle J \rangle$ is the point at which the Ni(II) moments saturate for fields lying in the easy-plane, while $g_{\text{eff}}\mu_BH_{\text{sat}} = 25\langle n\langle J \rangle \rangle$ is for fields parallel to the hard-axis [33]. Here, $n$ is the total number of effective nearest-neighbor exchange pathways and $\langle J \rangle$ is the average exchange strength. The D-value and $n\langle J \rangle$ were initially parameterized by finding the two critical fields $|\mu_0H_{\text{sat}}| = 32.0(3)$ T and $|\mu_0H_{\text{sat}}| = 54(1)$ T from a plot of $dM/dH$ vs. $\mu_0H$. Applying mean-field theory and assuming Heisenberg behavior for the Ni(II) ion, we found $D = 15(1)$ K and $n\langle J \rangle = 22.4$ (2) K.

The $M(H)$ data were successfully simulated using a Monte-Carlo algorithm based on an eight-spin cluster and complete powder-averaging for numerous spin orientations, yielding the following parameters: $D = 13.3$ K, $J = 10.4$ K, $f = 1.4$ K (solid line in Fig. 2a). Intra- ($J$) and interchain ($J'$) magnetic couplings are assigned to the respective Ni-FHF-Ni and Ni-pyz-Ni pathways. The small $J$ of $\approx 1-2$ K is typical of the exchange interaction encountered in several Ni(II)-pyz coordination polymers [10,33–35].

Inelastic neutron scattering (INS) measurements were made on a powder sample using a cold-neutron disk-chopper spectrometer. Subtracting data obtained in the paramagnetic state (20 K) from data obtained for $T \ll T_N$ (1.5 K) revealed a clear magnetic excitation centered at $\hbar\omega_0 \approx 3.4$ meV $\approx 39.4$ K (Fig. 2b).

### Table 3

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<td>—</td>
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<td>$\mu_BH_{\text{sat}}(T)$</td>
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<td>15.5(3)</td>
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* Average Ni-N bond length.

* Shortest of the two Ni-L distances.

* Obtained by independent simulation of $\chi(T, M/H)$ and inelastic neutron scattering data (see Ref [33]).

* Determined from $M(H)$ data; for tetragonal systems, $E = 0$ so $M(H)$ gives $D$ directly in those cases.

### Fig. 1

(a) Single crystal X-ray structure of $[\text{Ni(HF}_2\text{)(pyz)}_2\text{SbF}_6]$ (1) determined at $T = 100$ K. (a) Thermal ellipsoid plot (40% probability level) and atom labeling scheme. The Ni(II) center has local $D_{4h}$ symmetry. Symmetry codes: (i) $y - 1/2, -x + 1, -2z$; (ii) $-y + 1/2, x, z$; (iii) $-x + 1/2, -y + 1/2, z$; (iv) $-x + 1/2, -y + 1/2, z$; (v) $-x + 1/2, -y + 3/2, z$; (vi) $-y + 1, x + 1/2, -z$; (b) Polymeric 3D MOF-like structure. For simplicity, only the lower right quadrant shows the ‘nested’ C-H-F hydrogen bonds that tether the SbF$_6$ counterion in place.
excitation disappears above $T_N$ it must originate from spin-waves meaning that the total energy results from the sum of all magnetic contributions such that $S(Q,\omega) = D + 2J + 4\mu^2$. Simulating the spin-wave features (overlay plot in Fig. 2b), taking into account energy and wave-vector vectors, affords very good agreement for the parameters: $D = 13.3(1)$ K, $J = 10.4(3)$ K and $\mu = 1.4(2)$ K, in keeping with thermodynamic measurements [33].

For $k_BT < D$, the positive-$D$ value dictates an XY spin configuration of the Ni(II) magnetic moments within the ab-plane; i.e., normal to the Ni-FHF-Ni chains. Below $T_N = 12.2(1)$ K, the Ni moments adopt a collinear, 3D XY-AFM ordered ground-state as confirmed by symmetry analyses of neutron diffraction data [33]. At 1.5 K, a refined ordered moment of 2.03(7) $\mu_B$ was found as is typical of an ion containing two unpaired electrons. A fit of the order parameter gives a $\beta$-value of 0.141(1) which is consistent with a low-dimensional AFM magnetic structure.

Magnetic susceptibility [33] data obtained for a powder sample of 1 shows a broad maximum at 16 K and a subtle kink at $\approx 12$ K. The former features arise from short-range correlations along the Ni-FHF-Ni chains and the latter from long-range magnetic order between them. As no theoretical model exists to fit $\chi(T)$ for coupled $S = 1/2$ chains where $D$ and $J$ are of similar scale, we simulated these data (Fig. 2c) to arrive at $D = 11.8$ K, $J = 10.7$ K and $\mu = 0$ for the best values. The combination of experimental probes was necessary owing to the ambiguity in fitting the $\chi(T)$ derived from powder data with three variables $D$, $J$ and $\mu$.

3.1.3. Electronic structure calculations

The spin-density distribution, exchange constants [33] and ZFS have been computed for 1. It was previously shown that a portion of the Ni(II) magnetic moment ($\approx 0.2e$) was equally delocalized onto the F- and N-donor atoms. However, the close proximity of F-atoms within HF$_2$ provides nearly direct $p_z-p_z$ orbital overlap which leads to more effective spin exchange along Ni-FHF-Ni. The N-atoms of the pyz ring contain the bulk of the spin-density in the NiN$_4$ equatorial plane with only minute spin-density on the C-atoms [33]. This reduces the overall ability of pyz to efficiently mediate magnetic exchange along Ni-pyz-Ni, in contrast to the many Cu(II)-pyz variants [36–41].

Using CASSCF, the ZFS (this work) of the Ni(II) ion in 1 was computed for an uncharged mononuclear fragment [Ni(HF$_2$)$_2$(pyz)$_2$], ignoring counterions, but retaining the experimentally determined coordination geometry. The resulting ZFS-tensor was found to be diagonal in the Cartesian frame of the ligators and perfectly axial: $D = 16.9$ K and $E/D = 0$. By comparison, the calculated $D$ is consistent with the experimental $M(H)$ and INS values. The $E/D$ value should be strictly zero for a tetragonal system.

3.2. Structural and magnetic properties of NiF$_2$(pyz)$_2$·3H$_2$O (2)

3.2.1. Crystal structure at 297 K

The difficulty in growing single crystals of (2) for X-ray diffraction required implementation of X-ray powder methods (Fig. 3) to determine and refine the crystal structure of 2. Unlike the tetragonal members in the NiF$_2$(pyz)$_2$ series (X = Cl, Br, I) [34] the crystal structure of $X = F$ is monoclinic (I2/m). Pyrazine ligands link adjacent Ni(II) ions into square lattices (Fig. 4a) with $d$(Ni–Ni) = 7.024 (1) \AA and propagate along the (1 0 –1)-direction. Inversion centers occupy the center of each square and mirror planes (confined to the ac-plane) pass through Ni(II) ions located on opposite corners of the square. Glide planes run parallel to these mirrors and contain the midpoints of the pyz ligands.

Compressed NiF$_2$F$_2$ octahedra are composed of four equal $d$(Ni–N1) bonds of 2.117(2) Å and two axially-ligated F-atoms ($d$(Ni–F1) = 2.004(2) Å). Angular distortion around the Ni(II) center is small with F1–Ni–N1 being 90.3(1)°. Two-fold rotational symmetry about the F1-Ni-F1 axis negates the propeller-like disposition of pyz ligands observed in 1 [33,36]. This implies that for both Ni-pyz-Ni directions, the pyz ligands retain the same spatial arrangement and do not alternately tilt, a feature common in 1D chains such as $[Ni(gly)$_2$(pyz)$_2$(pyz)]$·5.21H$_2$O (3) but rare in 2D lattices. Each pyz is tilted away from the NiN$_4$ plane by 67.3(1)° and propagates along the (1 0 –1)-direction. Inversion centers occupy the center of each square and mirror planes (confined to the ac-plane) pass through Ni(II) ions located on opposite corners of the square. Glide planes run parallel to these mirrors and contain the midpoints of the pyz ligands.

Compressed NiF$_2$F$_2$ octahedra are composed of four equal $d$(Ni–N1) bonds of 2.117(2) Å and two axially-ligated F-atoms ($d$(Ni–F1) = 2.004(2) Å). Angular distortion around the Ni(II) center is small with F1–Ni–N1 being 90.3(1)°. Two-fold rotational symmetry about the F1-Ni-F1 axis negates the propeller-like disposition of pyz ligands observed in 1 [33,36]. This implies that for both Ni-pyz-Ni directions, the pyz ligands retain the same spatial arrangement and do not alternately tilt, a feature common in 1D chains such as $[Ni(gly)$_2$(pyz)$_2$(pyz)]$·5.21H$_2$O (3) but rare in 2D lattices. Each pyz is tilted away from the NiN$_4$ plane by 67.3(1)°. The trajectory of the Ni-pyz interaction is somewhat non-linear as indicated by Ni-N1...Ni$^{\text{II}}$ [175.6(1)°] which may limit efficiency of the magnetic exchange interaction (see below).

Fig. 3. $T = 297$ K X-ray powder diffraction data (●) for 2 along with the Rietveld refinement (—). Short vertical lines indicate expected Bragg positions whereas the difference plot ($I_{\text{obs}}-I_{\text{calc}}$) is shown as the blue line at the bottom. A handful of minor Bragg peaks belong to an unidentified impurity phase (*). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
Adjacent layers alternately pack in a staggered fashion in the direction normal to the F-Ni-F axis (Fig. 4b). This gives the closest interlayer $d(Ni/C1/C1/C1Ni)$ separation of 6.6744(1) Å which coincides with the $a$-axis unit cell dimension. Intercistral sites are occupied by HF or H$_2$O solvent molecules for which only the heavy atoms could be located during Rietveld refinement. The heavy atom distance of 2.436(2) Å is consistent with either $d(O/C1/C1/C1O)$ (typical range 2.363–2.46 Å; median = 2.413 Å) [42] or $d(F/C1/C1/C1F)$ (2.32–2.497 Å; median = 2.457 Å) as reported for several poly-HF adducts [42]. The final structural refinement for 2 settled on H$_2$O although the material may contain a mixture of HF/H$_2$O molecules, perhaps partially occupied (see Figs. S1 and S2), and this could slightly affect quantitative interpretation of the magnetometry data.

3.2.2. Magnetic susceptibility

The temperature-dependence of the magnetic susceptibility is presented in Fig. 5a. Upon cooling to 1.8 K, a rounded maximum was observed at 4.3 K with a subtle kink occurring near 2.3 K that may arise from long-range magnetic order (see below). At base temperature, the minimum value of $\chi(T)$ is 0.085 cm$^3$ mol$^{-1}$. In the inset of Fig. 5a, a Curie-Weiss fit of $1/\chi(T)$ reveals linear behavior over the range 50–300 K from which the $g$-factor of 2.28 (1) and $\theta_{CW} = -3.9(6)$ K were determined. The $g$-factor is typical of Ni(II) ions in this environment [8] and the negative Weiss constant indicates AFM coupling between the Ni(II) ions, likely within the square lattice. It is important to note that powder $\chi(T)$ data like these can be fitted equally well to several models containing only anisotropy terms or only exchange terms, but choosing one such
model leads to erroneous conclusions in the case where both $D$ and $J$ are present. An effective 2D fitting function of the susceptibility for an $S = 1$ Hamiltonian containing both $D$ and $J$ does not exist. With this limitation, we computed $J$ for 2 using DFT and found a value of 5.4 K which exceeds the typical upper limit of $\approx 1$–2 K expected for Ni-pyz-Ni pathways [10,33–35].

3.2.3. Pulsed-field magnetization

Pulsed-field magnetization $M(H)$ (calibrated using DC-field SQUID data) are shown in Fig. 5b. At the lowest temperatures, the measured $M(H)$ shows a slightly curved rise to a broad saturation, indicative of an $S = 1$ antiferromagnet with single-ion anisotropy. The saturation magnetization value of 2.32(6) $\mu_B$ per Ni$^{2+}$ ion is in good agreement with the $g$-factor determined from the susceptibility data.

Differential susceptibility ($dM/dH$) data (Fig. 5c) exhibits two characteristic fields, as expected for a polycrystalline material. Defining $\mu_b dH_{sat} = 5.1(1)$ T as the field at which $dM/dH$ begins to drop, and $\mu_b dH_{sat} = 15.5(3)$ T as the point at which $d^2M/dH^2$ tends to zero, we find that $n(f) = 1.95(4)$ K and $D = 8.0(5)$ K. However, the local Ni(II) site symmetry suggests a small $E$-term is possible. Assuming negligible interplane exchange coupling, $n = 4$ and $(f) = f_{pyz} = 0.49(2)$ K, which is similar to the Ni-pyz-Ni exchange energies found in several other square $[Ni(pyz)_2]^2+$ motifs [10,33–35].

As shown by an asterisk in Fig. 5c, an additional small feature is observed in the pulsed-field $dM/dH$ data at the lowest temperatures. The feature is not consistent with the spin-flop field estimated using the two observed saturation fields within an easy-axis model. However, analogous behavior was observed in $[Ni(H_2O)_2(pyz)_2][BF_4]_2$ wherein neutron diffraction data confirmed a 2D magnetic ground-state with Ni(II) moments confined to the $[Ni(pyz)_2]^2+$ square lattice [10].

3.2.4. Muon-spin relaxation

$\mu$SR asymmetry spectra of 2 collected in zero applied magnetic field are shown in Fig. 6a for temperatures of 1.7 K and 3.1 K. The spectrum at 1.7 K shows rapid oscillations that indicate long-range magnetic order [26]. No oscillations were seen in the 3.1 K data, suggesting that the magnetic order is destroyed by this temperature. We fit this data to the model shown in Eq. (2).

$$A(t) = A_1e^{-\gamma t}\cos(\gamma t + \phi) + A_2e^{-\gamma t} + A_3e^{-\gamma t}$$

Here, $A_1 = 0.062$, $A_2 = 0.045$, and $A_3 = 0.097$ are the temperature independent asymmetries of the three components, $\lambda_1$, $\lambda_T$, and $\lambda_B$ are their relaxation rates, $B$ is the internal field, $\gamma = 2\pi \times 135.5$ MHz T$^{-1}$ is the muon gyromagnetic ratio and $\phi = -29^\circ$ is a phase shift.

This fitting function has three components: an oscillating component ($A_1$) coming from the static magnetism, a relaxing component ($A_2$) typical of measurements of polycrystalline magnetic materials, and a weakly relaxing component ($A_3$) which we ascribe to a non-magnetic background such as might come from muons landing in the cryostat after missing the sample or failing to stop within it. Fig. 6b shows the temperature dependence of the internal field. The internal field falls off rapidly with increasing temperature, and above 2.2 K no oscillations can be resolved in the $\mu$SR data. This suggests that the magnetic transition occurs at $T_N \approx 2.1(1)$ K.

The spectra measured above the magnetic transition between $2.5 \leq T \leq 10$ K show little variation with temperature. An example spectrum measured at $T = 10$ K is shown in Fig. 6a and is well characterized by a combination of exponential relaxation and a non-relaxing background. This is typical of relaxation due to dynamic fluctuations of the electronic moments in a paramagnet. In materials of this type, positive muons would be expected to stop near electronegative fluorine atoms where they interact with the fluoride nuclei via a dipole–dipole interaction and give rise to a so-called F-μ spectrum, as seen in several related systems [43]. However, in 2 we do not resolve a clear F-μ spectrum. There is a slight change in the shape of the spectrum in Fig. 6a around 2 μs that might suggest a contribution from such a signal with a very low amplitude. This implies that the dynamic fluctuations of the electronic moments obscure any F-μ signal.

3.3. Structural and magnetic properties of $[Ni(gly)_2(pyz)]5.21H_2O$ (3)

3.3.1. Crystal structure

The local structure about the Ni(II) center in 3 is composed of two trans-O-atoms, two trans-N-atoms from chelated gly ligands and two N-atoms belonging to pyz (Fig. 7a). Established by average $d(Ni-N)$ and $d(Ni-O)$ distances of 2.097(4) and 2.059(3) Å, respectively, we assign the four N-atoms to the equatorial plane and Ni(II) moments confined to the Ni(pyz)$_2$ square lattice [10].

Fig. 6. (a) Measured $\mu$SR spectra (●) for 2 obtained at 1.7, 3.1 and 10 K. Solid lines are fits to the data as described in the text. (b) T-dependence of the internal field $B$ extracted by fitting the data in (a) to Eq. (2).
Ni-N3–N4 angle is 178.7(2)°. Neighboring chains stagger along the b-axis and pack to form planar sheets within the bc-plane as shown in Fig. 7b. The closest d(Ni–Ni) separation is 7.054(1) Å and only slightly longer than the intrachain distance. There are four such sheets per unit cell which stack along the a-axis. Channels between adjacent sheets are alternately filled by a variable number of H2O molecules that are extensively connected through O–H bonds ranging in length from 1.85 to 2.65 Å.

3.3.2. Magnetic susceptibility

The χ(T) data rises as the temperature is lowered and exhibits a maximum at ≈ 2.5 K, in keeping with the presence of weak magnetic exchange. As plotted in the inset of Fig. 8a, a Curie-Weiss model was used to fit to 1/χ(T) above 50 K to afford the parameters: $g = 2.23(1)$, $\theta_{\text{CW}} = -1.3(3)$ K and a temperature-independent term $\chi_0 = 1.2(2) \times 10^{-5}$ m³ mol⁻¹. The small $\theta_{\text{CW}}$ value is consistent with the expectedly weak AFM exchange coupling along Ni-pyz-Ni.

3.3.3. Pulsed-field magnetization

Pulsed-field $M(H)$ data were calibrated using SQUID data and found to saturate at 2.3(1) $\mu_B$ consistent with the g-factor obtained from the $\chi(T)$ data (Fig. 8a). The powder differential susceptibility (Fig. 8b) shows two critical fields; $\mu_0 H_{\text{sat}}$ at 1.8(2) T and saturation $\mu_0 H_{\text{sat}}$ at 12.5(5) T. Within the easy-plane model these fields imply $n(\tilde{J}) = 1.4(2)$ K and $D = 8.0(6)$ K. The chelating gly ligand induces a low symmetry of the Ni(II) center which will likely yield a non-zero $E$-term, thus 8.0 K is an upper limit on $D$.

3.4. Structural and magnetic properties of Ni(AF₆)(vinim)$_4$ [A = Ti (4), Zr (5)]

3.4.1. Crystal structure

While Ni(SiF₆)(vinim)$_4$ was reported some years ago, its crystal structure was not determined but inferred from that of the structurally-characterized Co(II)-analog [44]. We synthesized the [TiF₆]$_2^2$ (4a and 4b) and [ZrF₆]$_2^2$ (5) congeners and show via X-ray diffraction methods that they are structurally similar to Co(SiF₆)(vinim)$_4$. The structures were determined by Rietveld refinement of synchrotron powder diffraction (4a; Fig. 9) and laboratory-based single crystal X-ray diffraction data (4b and 5).

The difference in crystalline properties are attributed to ordered (4a and 5) and disordered (4b) vinim ligands. For ordered vinim molecules (Fig. 10a), even partially, a lower symmetry permits finite intensity for $h + k + l$ odd Bragg reflections (* in Fig. 9; inset) and the relevant space group is $P4_2/n$. Alternatively, positional disorder (Fig. 10b) of the vinim ligands affords higher crystal symmetries and extinctions in the X-ray diffraction pattern conducive to space group $I4/m$. Fig. 9 compares the experimental data to the predicted pattern for each space group assignment. Crushing crystals of 4b into a fine powder leads directly to 4a (see Fig. S3).

The differing structural symmetries for both forms of Ni(TiF₆)(vinim)$_4$ reveal key differences with regard to the pseudo-octahedral NiN₄F₂ environment with F-atoms located on axial sites. For the case of $P4_2/n$ (4a), there are four equivalent Ni-N1 bond distances of 2.005(4) Å and two longer Ni-F1 distances of 2.076(3) Å. The bond angles making up the Ni coordination sphere are nearly ideal with the largest distortions being 88.4(3)° and 176.7(3)°. In the $I4/m$ system (4b), the four-fold axis runs through the F-Ni-F axis which generates four equivalent Ni-N1 distances of 2.070(1) Å and two equivalent Ni-F1 bonds of 2.072(1) Å. Thus, the Ni coordination sphere may essentially be described as isotropic. All of the F1-Ni-F1, F1-Ni-N1 and N1-Ni-N1 bond angles are ideal at 90 and 180°.

In 5, the Ni(II) and Zr(IV) centers have two-fold symmetry with respect to the c-axis. Atom F1 occupies the glide plane perpendicular to the c-direction. The Ni(II) center is isotropic with equal $d$(Ni-N1) and $d$(Ni-F1) bond distances of 2.078(1) Å whereas the $d$(Zr-F1) and $d$(Zr-F2) bond lengths are slightly different at 2.029 Å.
and 1.995(1) Å, respectively. Bond angles around each metal center deviate from the ideal octahedral angles with the most distorted being 88.39(1)° for F1-Ni-N1 and 88.04(1)° for F1-Zr-F2. Trans-N-Ni-N bond angles are non-linear at 176.78(3)° while the equatorial F-Zr-F bond angle is 176.08(2)°. The ethylene portion of each vinim ligand occupies roughly the same plane as the imidazole ring to which it is attached.

The [ZrF6]2⁻ ion links [Ni(vinim)4]2+ units through F1-atoms to afford linear 1D chains with d(Ni–Zr) distances of 4.107(1) Å (Fig. 10a). A comparison among the [AF6]2⁻ derivatives yields d(Ni–Ni) separations that vary from 7.89890(2) Å (4a) to 8.1946 (7) Å (5), consistent with an increase in M(IV) ionic radius. Within a chain, one trans-pair of vinim ligands form bifurcated C–H···F hydrogen bonds, notably C1–H1···F2 [d(H1···F2) = 2.23(1) Å; C1–H1···F2 = 174.7(2)°] and C3–H3···F2 [d(H3···F2) = 2.56(1) Å; C3–H3···F2 = 171.7(2)°], with one [ZrF6]2⁻ unit as shown by orange dashes in Fig. 10a while the remaining trans-pair interacts with the other [ZrF6]2⁻ moiety.

Adjacent chains are staggered by 1/2 c leading to large inter-chain d(Ni–Ni) distances of no less than 9.757(1) Å. Weak van der Waals interactions hold the chains together but do not provide effective exchange pathways. Thus, the chains may be described as being magnetically isolated.

3.4.2. Magnetic susceptibility

Powdered susceptibility data for both compounds shows a slow rise to a plateau-like feature that develops at temperatures below T < 10 K (Fig. 11a and b) and resembles the data expected for an
ensemble of $S = 1$ moments with single-ion anisotropy, but no significant exchange interactions [10]. Both materials are fitted well by a $D$-only powder-average model [10,45] along with a small $\chi_D$.

For compound 4a, the fit is good and returns estimates of $D = 24.9(1)$ K, $g = 2.132(3)$ and $\chi_D = 1.5(1) \times 10^{-9}$ m$^3$ mol$^{-1}$. This value of $D$ is in reasonable agreement with the ESR data (see below), however, the $g$-value is a little smaller than expected for Ni(II) ions in this local environment and lower than the powder average ESR value of $g = 2.21$. Fitting the inverse susceptibility to a Curie-Weiss law, inset of Fig. 11a, yielded $g = 2.28(1)$, $\theta_{CW} = -3.6(2)$ and $\chi_0 = 3(1) \times 10^{-10}$ m$^3$ mol$^{-1}$.

For 5, the $D$-only model fits the $\chi(T)$ data well over the entire $T$-range but with a slight departure at low temperatures. The parameters estimated from the fit are $D = 18.5(1)$ K, $g = 2.18(1)$ and $\chi_0 = 1.3(2) \times 10^{-9}$ m$^3$ mol$^{-1}$, in reasonable agreement with the ESR (see below). A fit of $1/\chi(T)$ between 50 and 300 K yielded a good agreement for the parameters $g = 2.19(1)$, $\theta_{CW} = 1.2(9)$ K and $\chi_0 = 5.1(9) \times 10^{-9}$ m$^3$ mol$^{-1}$.

3.4.3. Pulsed-field magnetization

In both compounds, we would expect to see a bump in $dM/dH$ corresponding to the field at which the $m_z = 1$ energy level crosses the $m_z = 0$ ground state energy level for fields applied along the magnetic hard-axis, as described in [10,46]. However no clear features are observed in the data (inset to Fig. 11c). It is possible that a significant amount of the polycrystalline sample reorients during a pulsed-field measurement, aligning the easy-plane with the applied field. This would reduce the size of the feature observed at the level crossing for subsequent pulses.

3.4.4. Electron-spin resonance

The Ti-complex 4a exhibits high-field ESR spectra of poor quality however, estimates of $g_z$ and $D$-values [2.2(2) and 23.8(5) K, respectively], can be made. Similar (although better quality) spectra were obtained for 5, from which $g_z = 2.22(1)$ and $D = 20.0(5)$ K were determined. Electronic structure calculations give $D = 18.1$
and 16.9 K for 4a and 5, respectively, which are in keeping with the experimental trend.

3.5. Structural and magnetic properties of [Ni(SiF₆)(mepz)(H₂O)]·H₂O (6)

3.5.1. Crystal structure

Reaction between NiSiF₆ and four equivalents of 4-methylpyrazole leads to deep blue crystals of 6. The material crystallizes in the monoclinic space group Cc with Z = 4. From Fig. 12 it can be seen that neutral molecules of Ni(SiF₆)(mepz)(H₂O) feature axial sites occupied by [SiF₆]²⁻ \[d(Ni-F1) = 2.130(2) \text{ Å}\] and H₂O ligands \[d(Ni-O1) = 2.063(2) \text{ Å}\]. Equatorial Ni-N distances range from 2.065 (3) to 2.105(3) Å. Bond angles around the Ni(II) center deviate appreciably from the ideal octahedral angles with N5-Ni-O1 and N5-Ni-N1 being the most distorted at 94.4(1)° and 174.6(1)°, respectively. The distortive behavior arises from intramolecular hydrogen bond formation between pyrazole N-H moieties and equatorial F-atoms of the [SiF₆]²⁻ anion. Orange dashed lines in Fig. 12 represent these interactions which have distances of 1.88 (5)-2.08(5) Å and N–H···F bond angles of roughly 167(4)-173(4)°.

Owing to intermolecular O1–H1B···F4 hydrogen bond interactions, the molecules pack to form pseudo-1D chains \[d(H1B-F6) = 1.92(5) \text{ Å}\; \text{and bond angle} = 165(4)°\]. Atom H1A interacts with the lattice H₂O (not shown in Fig. 12). Van der Waals interactions hold the chains together leading to negligible magnetic couplings.

3.5.2. Magnetic susceptibility

The powder DC susceptibility of 6 (Fig. 13a) rises as the temperature is lowered until a plateau is reached below 3 K. The data are suggestive of a system with little or no exchange coupling and easy-plane anisotropy that neutral molecules of Ni(SiF₆)(mepz)(H₂O) feature axial sites occupied by [SiF₆]²⁻ \[d(Ni-F1) = 2.130(2) \text{ Å}\] and H₂O ligands \[d(Ni-O1) = 2.063(2) \text{ Å}\]. Equatorial Ni-N distances range from 2.065 (3) to 2.105(3) Å. Bond angles around the Ni(II) center deviate appreciably from the ideal octahedral angles with N5-Ni-O1 and N5-Ni-N1 being the most distorted at 94.4(1)° and 174.6(1)°, respectively. The distortive behavior arises from intramolecular hydrogen bond formation between pyrazole N-H moieties and equatorial F-atoms of the [SiF₆]²⁻ anion. Orange dashed lines in Fig. 12 represent these interactions which have distances of 1.88 (5)-2.08(5) Å and N–H···F bond angles of roughly 167(4)-173(4)°.

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Pulsed-field measurements for a powder sample rises slowly to saturation (Fig. 13b) in keeping with a large D. The data were calibrated using the SQUID results and show that 6 saturates at 2.25 (1) \(\mu_B\); this suggests \(g = 2.25(1)\), in excellent agreement with the value of \(g\) obtained from the \(\chi(T)\) data. The differential magnetization at 0.58 K drops smoothly until a bump emerges at \(\approx 8\) T. This is characteristic of an easy-plane Ni(II) compound that exhibits negligible magnetic interactions [10]. The data continue to decline beyond the bump. The position of \(\mu_BH_s\) was found from the midpoint of the peak derivative shape in the \(d^2M/dH^2\) data and was located at \(\mu_BH_s = 7.8(6)\) T; using the results from [10], an estimate of \(\sqrt{D^2 - E^2} = 11.8(7)\) K was obtained which agrees very well with the fit of \(\chi(T)\).

3.5.3. Pulsed-field magnetization

Pulsed-field measurements for a powder sample rises slowly to saturation (Fig. 13b) in keeping with a large D. The data were calibrated using the SQUID results and show that 6 saturates at 2.25 (1) \(\mu_B\); this suggests \(g = 2.25(1)\), in excellent agreement with the value of \(g\) obtained from the \(\chi(T)\) data. The differential magnetization at 0.58 K drops smoothly until a bump emerges at \(\approx 8\) T. This is characteristic of an easy-plane Ni(II) compound that exhibits negligible magnetic interactions [10]. The data continue to decline beyond the bump. The position of \(\mu_BH_s\) was found from the midpoint of the peak derivative shape in the \(d^2M/dH^2\) data and was located at \(\mu_BH_s = 7.8(6)\) T; using the results from [10], an estimate of \(\sqrt{D^2 - E^2} = 11.8(7)\) K was obtained which agrees very well with the fit of \(\chi(T)\).

3.5.4. Electron-spin resonance

Low-temperature ESR spectra recorded for powdered 6 were obtained over the frequency range 100 ≤ ν ≤ 326.4 GHz (Fig. 13a). The 108, 208 and 326.4 GHz spectra were measured at 5 K while all other spectra were obtained at the base temperature of the cryostat (≈ 3 K). Resonances corresponding to high-field \(z(\gamma_z)\) and \(y(\gamma_y)\) transitions were observed in the 104 and 108 GHz sweeps. The high-field \(z(\gamma_z)\) transition is the most intense resonance for \(ν ≤ 208\) GHz and gives a direct measure of \(D\) by linearly extrapolating the position of the transition at different \(ν\) back to zero. The zero-field intercept occurs at \(≈ 230\) GHz, which corresponds to a zero-field splitting energy of \(≈ 11\) K. The 108 GHz and 208 GHz sweeps were also measured at 30 K. Fig. 14 shows that the \(X\) and \(Y\) features, seen in the 30 K, 208 GHz spectrum at 9.2 T and 10.2 T, respectively, become frozen out when \(T\) is lowered to 5 K. This is indicative of easy-plane anisotropy in 6. The \(\gamma_z\) transition is only observed in the high-temperature data (Inset of Fig. 14b), providing further evidence that \(D > 0\). The half-field \(z(\alpha_z)\) transition also figures prominently in the low-frequency sweeps. For \(ν ≥ 230\) GHz, the low-field \(x(\alpha_x)\), \(y(\alpha_y)\) and \(z(\alpha_z)\) transitions are observed. Apparent features that likely correspond to the half-field \(x(\alpha_x)\) and \(y(\alpha_y)\) transitions are positioned to the high-field side of \(\beta_z\) in the 326 GHz spectra, though spectral noise makes it difficult to accurately resolve their positions.

The observed transitions were plotted and fitted to a D- and E-only model (Fig. 15). The parameters \(D = 1.145(2)\), \(E = 0.49(1)\), \(g_x = 2.240(7)\), \(g_y = 2.228(5)\) and \(g_z = 2.158(5)\) were extracted, and the model is in good agreement with the data. A 326 GHz simulation using these parameters at 5 K is shown in Fig. 15 and recreates the \(\beta_x\) and \(\beta_y\) transitions. The simulated \(\beta_z\) resonance at 3 T is also in good agreement with the data, whilst the \(\alpha_x\) and \(\alpha_y\) resonances are shown to lie in the noisy region to the high-field side of \(\beta_z\), confirming the above interpretation. The fact that \(g_y > g_x\) is consistent with easy-plane anisotropy and a value of \(\lambda = 279\) K is obtained for the spin–orbit coupling parameter. This is of the same order of magnitude as that anticipated for Ni(II) ions [8]. Thus, the parameters obtained from the magnetometry and ESR measurements are in very good agreement.

Fig. 12. Crystal structure and atom labeling scheme for [Ni(SiF₆)(mepz)(H₂O)]·H₂O (6). Lattice H₂O and most mepz H-atoms have been omitted for clarity. Intra- and intermolecular H-bonds are delineated by orange and black dashes, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
3.6. Structural and magnetic properties of NiF$_2$(OHpy)$_4$ (7)

3.6.1. Crystal structure

Akin to the previously reported chloride complex [47], the fluoride compound also crystallizes in the orthorhombic space group Pccn with four discrete molecules per unit cell (Fig. 16a). Each NiN$_4$F$_2$ octahedron is slightly compressed with the Ni(II) ion possessing two-fold rotational symmetry along the F$_1$-Ni-F$_1$ axis. Four OHpy molecules coordinate to the Ni equatorial sites with an average d(Ni-N) bond distance of 2.107(2) Å. The two axial Ni-F bonds are equal at 2.055(2) Å. The distortion exhibited by the NiN$_4$F$_2$ octahedron is noted by the F$_1$-Ni-N$_1$ and F$_1$-Ni-F$_1$ bond angles of 86.16(7) and 177.11(8)/C176, respectively, which deviate appreciably from the ideal 90 and 180/C176 angles. Bond distances and angles within the pyOH ligand are typical of this molecule. Of note is the coplanarity of the hydroxyl substituent relative to the pyridine ring.

Within the unit cell (Fig. 16b), it can be seen that the NiF$_2$(OHpy)$_4$ molecules pack in two unique orientations relative to one another. This allows intermolecular O-H...F hydrogen bonds to link molecules into a quasi-2D lattice, with the shortest intra-layer d(Ni–Ni) separations being 7.377 and 9.179 Å. Each F$_1$-atom forms bifurcated H-bonds with H$_1$ and H$_2$ at distances of 1.775 and 1.725 Å, respectively, and nominal bond angles O$_1$-H$_1$...F$_1$ = 161.4° and O$_2$-H$_2$...F$_1$ = 169.1°.

3.6.2. Magnetic susceptibility

SQUID magnetometry data in the form of $\chi(T)\mu_B$ per Ni$^{2+}$ are shown in Fig. 17a and are typical of a system of non-interacting anisotropic...
$S = 1$ moments. The $\chi(T)$ data were modelled over the $1.8 \leq T \leq 300$ K range using a conventional powder-average model describing the magnetocrystalline anisotropy for an $S = 1$ ion; $J = J_0 = 0$ is assumed in Eq. (1) [10,46]. Intermolecular H-bond mediated exchange is likely to be very weak in this material. From a least-squares fit (solid line in Fig. 17a), we obtain $g = 2.16$, $D = 12.3(5)$ K, $E = 1.9(1)$ K and $v_0 = 4.3 \times 10^{-9}$ m$^3$ mol$^{-1}$ (fixed).

3.6.3. Magnetization

Pulsed-field $M(H)$ vs $\mu_B H$ data were measured at several temperatures between 0.5 and 10 K and at fields up to 30 T; data are shown in Fig. 17b. At the highest fields measured, $M$ saturates close to 2.1–2.2 $\mu_B$ as expected from the $g$-value obtained from the $\chi(T)$ data. The absence of a spin-flop transition is consistent with $D > 0$ [11]. Applying the easy-plane model to the weak bump seen in $dM/dH$ [11], we estimate $\sqrt{D^2/E^2} = 12.2(3)$ K which is in very good agreement with the $\chi(T)$ result.

3.6.4. Electron-spin resonance

Spectra measured at 10 K reveal signals indicative of isolated Ni(II) complexes (blue line in Fig. 18a). Simulating these data, of which examples taken at 305.1 and 630.9 GHz are shown as the red line in Fig. 18a, we find $g_\parallel = 2.205(5)$, $g_\perp = 2.220(3)$, $g_z = 2.151(5)$, $D = 12.36(1)$ K and $E = 1.16(1)$ K. The anisotropy values are in good agreement with those obtained from magnetometry measurements. The field-frequency profile is shown in Fig. 18b where it can be seen that the observed values occur at the expected resonances determined by the $g$, $D$ and $E$-parameters.

4. Conclusions

For the $S = 1$ Ni(II) coordination complexes studied here, including molecules and polymers, we showed that $D > 0$ can be forecast with good accuracy for six-coordinate trans-ligated NiN$_4$F$_2$, NiN$_4$O$_2$ and NiN$_4$OF systems. The Ni-N bond lengths are equal to or slightly longer than axial Ni-L giving isotropic or slightly compressed octahedra, respectively. A qualitative model based on the $|d(Ni-N_{ax})|/d(Ni-N_{eq})$ ratio shows an overall good correlation with the magnitude of $D$ (Fig. 19) and, from the spectrochemical series, the anticipated ligand-field strength is: $F \approx HF_2 \ll H_2O \ll gly <$ amines.
donor-atom strength grows, $D$ becomes increasing more positive and we observe the largest values for NiN$_4$F$_2$; e.g., Ni(TiF$_6$)(vinim)$_4$ (4a), $D = 25$ K. Two other NiN$_4$F$_2$ compounds included in Fig. 19 are [NiF$_2$(lut)$_4$]$\cdot$H$_2$O (8) and Ni(HF$_2$)$_2$(lut)$_4$ (9) (lut = 3.5-lutidine) which are described in detail elsewhere [48]. However, their smaller $D$-values are attributed to a larger difference in Ni-N and Ni-F bond lengths. For [Ni(SiF$_6$)$(\text{mepz})_4$(H$_2$O)]$\cdot$H$_2$O (6), replacing one F-donor with H$_2$O leads to a lower site symmetry about the Ni(II) ion and reduces $D$ by nearly 50%. [Ni(gly)$_2$(pyz)]$_2$ (3) exhibits the smallest $D$ of the materials studied which may be due, in part, to the close proximity of gly and pyz in the spectrochemical series.

The most striking observation in Fig. 19 is that $d$($\text{Ni-L}_{ax}$)/$d$(Ni-N$_{eq}$) deviates by only $\pm$0.05 compared to the isotropic case ($=1.00$) and yet, significant variation in $D$ was found. This further highlights the extreme sensitivity of $D$ to the ligand-field surrounding the Ni(II) ion. The fact that [Ni(gly)$_2$(pyz)]$_2$ $\cdot$5.21H$_2$O (3), [Ni(SiF$_6$)$(\text{mepz})_4$(H$_2$O)]$\cdot$H$_2$O (6) and [Ni(HF$_2$)$_2$(lut)$_4$]$\cdot$BF$_4$$_2$ (11) do not fit the correlation shown in Fig. 19 (solid line) suggests that other electronic factors such as the donor-atom electronegativity, $\pi$-character of Ni-N and Ni-L bonds, orbital reduction factors, etc., may be important and we are pursuing this further. Collectively, this work demonstrates an efficient and predictive model of easy-plane anisotropy in bespoke S = 1 Ni(II) quantum magnets.

CRediT authorship contribution statement

Jamie L. Manson: Conceptualization, Methodology, Visualization, Writing - original draft, review & editing, Supervision, Project administration, Funding acquisition. Zachary E. Manson: Resources, Investigation, Validation. Ashley Sargent: Resources, Investigation, Validation. Danielle Y. Villa: Resources, Investigation, Validation. Nicole L. Etten: Resources, Investigation, Validation. William J.A. Blackmore: Investigation, Formal analysis, Visualization, Writing - original draft. Samuel P.M. Curley: Investigation, Formal analysis, Visualization, Writing - original draft. Robert C. Williams: Investigation, Formal analysis, Visualization, Writing - original draft. Jamie Brambleby: Investigation, Formal analysis, Visualization, Writing, Paul A. Goddard: Methodology, Visualization, Writing, review & editing, Supervision, Data curation, Funding acquisition. Andrew Ozarowski: Investigation, Formal analysis, Visualization, Murray N. Wilson: Investigation, Formal analysis, Visualization, Writing, - review & editing, Data curation, Funding acquisition. Benjamin M. Huddart: Investigation, Formal analysis, Visualization, Writing - review & editing, Data curation, Funding acquisition. Tom Lancaster: Investigation, Formal analysis, Visualization, Writing, review & editing, Data curation, Funding acquisition. Roger D. Johnson: Methodology, Investigation, Formal analysis, Software, Validation. Stephen J. Blundell: Investigation, Formal analysis, Visualization, Writing, review & editing, Data curation, Funding acquisition. Jesper Bendix: Methodology, Software, Validation. Kraig A. Wheeler: Formal analysis, Software, Validation, Funding acquisition. Saul H. Lapidus: Investigation, Formal analysis, Serena Birnbaum: Investigation, Formal analysis, John Singleton: Investigation, Formal analysis, Methodology, Visualization, Writing - review & editing, Supervision, Data curation, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Fig. 18. T = 10 K ESR data for 7. (a) Measured (blue line) and simulated (red line) spectra at $f = 350.1$ and 630.9 GHz. (b) field-frequency profile with experimental data and calculated resonances shown as points and colored lines, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 19. Magnetostructural $\alpha$-correlation for compounds 1–7. Data for 8–11 are from Refs. [10,48]. Compounds 3, 10 and 11 consist of NiN$_4$O$_2$ coordination spheres while that of 6 is NiN$_4$OF.
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Appendix A. Supplementary data

CCDC 1956442–1956430 & 1956865 contains the supplementary crystallographic data for this paper. This data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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