

# [Cu(HF<sub>2</sub>)(pyz)<sub>2</sub>]BF<sub>4</sub> (pyz = pyrazine): long-range magnetic ordering in a pseudo-cubic coordination polymer comprised of bridging HF<sub>2</sub><sup>-</sup> and pyrazine ligands†

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[Cu(HF<sub>2</sub>)(pyz)<sub>2</sub>]BF<sub>4</sub> consists of rare  $\mu_{1,3}$  bridging HF<sub>2</sub><sup>-</sup> anions and  $\mu$ -pyrazine ligands leading to a 3D pseudo-cubic framework that antiferromagnetically orders below 1.54(1) K.

The bifluoride ion, *i.e.* HF<sub>2</sub><sup>-</sup>, contains a two-coordinate H-atom exhibiting the strongest known hydrogen bond.<sup>1</sup> Molecular orbital theory<sup>2</sup> and various structural investigations<sup>3</sup> suggest that this molecule can be best described as a hydrogen cation that is bridging two fluoride anions as in F<sup>-</sup>⋯H<sup>+</sup>⋯F<sup>-</sup>. Resonance modes consisting of coordinate covalent interactions such as F–H⋯F<sup>-</sup> and F<sup>-</sup>⋯H–F may also be important.<sup>2</sup> In the KHF<sub>2</sub> and NH<sub>4</sub>HF<sub>2</sub> salts, the H⋯F bond lengths in the HF<sub>2</sub><sup>-</sup> anion are equivalent at 1.14 Å, which is substantially shorter than the H⋯F hydrogen bond distance of 1.57 Å found in the solid phase of HF.<sup>4</sup>

Pyrazine (pyz) has been extensively utilized as a neutral bridging ligand in the self-assembly of polymeric networks comprised of transition metal cations.<sup>5,6</sup> Furthermore, pyrazine is well known to facilitate long-range antiferromagnetic ordering with a range of exchange coupling constants. Two important examples, Cu(NO<sub>3</sub>)<sub>2</sub>(pyz)<sup>5a</sup> and Cu(ClO<sub>4</sub>)<sub>2</sub>(pyz)<sub>2</sub>,<sup>5b</sup> which form one-dimensional (1D) chains and two-dimensional (2D) square lattices, respectively, have been identified as model low-dimensional *S* = ½ antiferromagnets. In a more recent example, bulk magnetic ordering has been reported in 2D layered Fe(NCS)<sub>2</sub>(pyz)<sub>2</sub> which exhibits Ising-like magnetic behavior.<sup>6</sup>

Much of our recent work has focused on the use of pyrazine ligands and a variety of potentially coordinating anions such as dicyanamide (dca).<sup>7</sup> We have begun to employ the HF<sub>2</sub><sup>-</sup> anion in a similar role so as to study its coordinative properties and its ability to mediate spin exchange interactions between open-shell metal cations. Our design strategy is purposeful in that we are

directly utilizing HF<sub>2</sub><sup>-</sup> as a building block under mild conditions while previously reported compounds fortuitously generate this anion *in situ* when aqueous HF is used as a solvent.<sup>3a,8</sup> While pipzH<sub>2</sub>[MnF<sub>4</sub>(HF<sub>2</sub>)] (pipz = piperazine) contains a bridging bifluoride anion, no magnetic interaction was observed.<sup>3a</sup> Under appropriate conditions, we believe that HF<sub>2</sub><sup>-</sup> may in fact be a suitable superexchange ligand and warrants further study. To this end, we have synthesized the novel coordination polymer, [Cu(HF<sub>2</sub>)(pyz)<sub>2</sub>]BF<sub>4</sub>, by aqueous reaction of stoichiometric amounts of copper(II) tetrafluoroborate hydrate, ammonium bifluoride, and pyrazine.<sup>†,9</sup>

The crystal structure of [Cu(HF<sub>2</sub>)(pyz)<sub>2</sub>]BF<sub>4</sub> has been determined using conventional X-ray diffraction methods.‡ Each Cu<sup>2+</sup> center occupies a 422 symmetry site and lies at the center of a slightly elongated octahedron with four Cu–N and two Cu–F(2) bond distances of 2.040(4) and 2.207(4) Å, respectively. Owing to the high symmetry of the Cu site, all F(2)–Cu–N, N–Cu–N, and F(2)–Cu–F(2') bond angles are regular, *i.e.* 90 and 180°. The HF<sub>2</sub><sup>-</sup> anion features a symmetrically placed hydrogen atom located at a 422 site with H–F and F⋯F bond distances of 1.102(4) and 2.205(4) Å, respectively. Additionally, the H(2)–F(2)–Cu bond angle is 180° while C–N–Cu is 121.3(2)°. All intramolecular bond distances and angles associated with the pyrazine ligand are in agreement with reported values.<sup>5,6</sup>

The extended structure of [Cu(HF<sub>2</sub>)(pyz)<sub>2</sub>]BF<sub>4</sub> is polymeric and consists of a three-dimensional (3D) framework shown in Fig. 1. Infinite 2D [Cu(pyz)<sub>2</sub>]<sup>2+</sup> sheets are formed in the *ab*-plane that are connected along the *c*-axis by linearly bridging  $\mu_{1,3}$ -HF<sub>2</sub><sup>-</sup> anions. By comparison, Cu(ClO<sub>4</sub>)<sub>2</sub>(pyz)<sub>2</sub> has a similar 2D network, however, the ClO<sub>4</sub><sup>-</sup> anions do not bridge between the 2D [Cu(pyz)<sub>2</sub>]<sup>2+</sup> sheets but rather are terminal groups.<sup>5b</sup> The ClO<sub>4</sub><sup>-</sup> anions pack in between the layers in such a way as to cause the sheets to be mutually staggered. From Fig. 1, it can be seen that the pyrazine ligands in [Cu(HF<sub>2</sub>)(pyz)<sub>2</sub>]BF<sub>4</sub> are all tilted out of the *ab*-plane by 59.4(2)° in a pattern consistent with the 4-fold rotation symmetries of the copper sites. A similar rotation of pyz rings along *M*–pyz–*M* bridges has been reported in quasi-2D [Cu(NO<sub>3</sub>)(pyz)<sub>2</sub>]PF<sub>6</sub>.<sup>10</sup> Because the Cu⋯Cu separations along the Cu–pyz–Cu and Cu–FHF–Cu linkages are very similar [6.8519(3) and 6.6193(4) Å, respectively], the structure may be described as pseudo-cubic. The BF<sub>4</sub><sup>-</sup> anions occupy the body-centered positions within each “cubic” pore, with the B-atom resting on a  $\bar{4}$  2m site.

The magnetic properties of [Cu(HF<sub>2</sub>)(pyz)<sub>2</sub>]BF<sub>4</sub> were probed using a Quantum Design MPMS-7 SQUID magnetometer and

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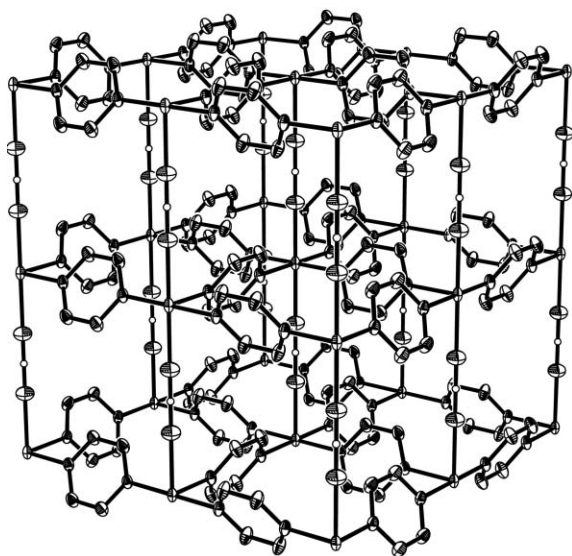
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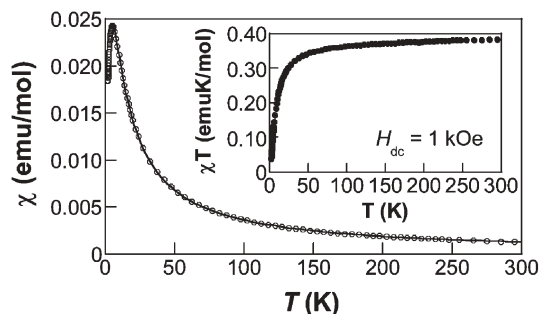


**Fig. 1** Crystal structure of  $[\text{Cu}(\text{HF}_2)(\text{pyz})_2]\text{BF}_4$  at 295 K. Pyrazine H-atoms and  $\text{BF}_4^-$  anions have been omitted for clarity. Thermal ellipsoids are drawn at the 35% probability level.

data collected upon warming between 2 and 300 K. The main plot of Fig. 2 shows  $\chi$  vs.  $T$  while  $\chi T$  vs.  $T$  is plotted in the inset. At room temperature, the value of  $\chi T$  is 0.367 emuK/mol, which is slightly smaller than the expected value of 0.375 emuK/mol for isolated spin- $1/2$   $\text{Cu}^{2+}$  cations. Upon cooling,  $\chi T$  decreases continuously until  $\sim 50$  K, below which it falls off much more rapidly owing to increasing antiferromagnetic correlations between  $\text{Cu}^{2+}$  sites.

$\chi$  reaches a broad maximum at 5.5 K, which is likely due to short-range magnetic interactions. Below  $\chi_{\text{max}}$ , the data decrease continuously to the lowest measured temperature of 2 K, reaching a value of 0.017 emu/mol. The observed broad maximum, albeit at a lower temperature, is very similar to that found for 2D  $\text{Cu}(\text{ClO}_4)_2(\text{pyz})_2$ .<sup>5b</sup> A Curie–Weiss fit of  $\chi$  between 6 and 300 K yielded  $g = 2.048(1)$  and  $\theta = -8.1(1)$  K which indicates antiferromagnetic coupling between the spin- $1/2$   $\text{Cu}^{2+}$  ions in the title compound. Within the limited temperature range of our instrumentation, there was no evidence for long-range magnetic ordering (LRO) above 2 K.

The magnetic  $\text{Cu } 3d_{x^2-y^2}$  orbital of each  $\text{CuN}_4\text{F}_2$  octahedron lies in the  $\text{CuN}_4$  plane so that the spin exchange interactions between neighboring  $\text{Cu}^{2+}$  ions occur through the  $\sigma$ -bonded pyz ligands. Therefore to a first approximation, the magnetic structure of  $[\text{Cu}(\text{HF}_2)(\text{pyz})_2]\text{BF}_4$  can be described by a 2D square lattice. A



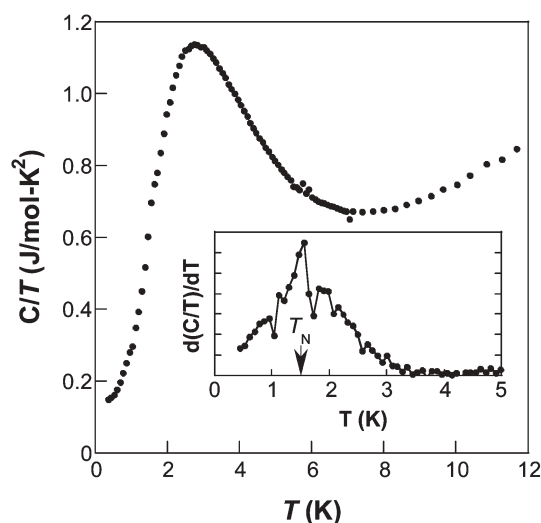
**Fig. 2** Plots of  $\chi$  (main) and  $\chi T$  (inset) for  $[\text{Cu}(\text{HF}_2)(\text{pyz})_2]\text{BF}_4$ .

least-squares fit of  $\chi$  to a spin- $1/2$  Heisenberg square lattice antiferromagnet<sup>11</sup> ( $H = -J\sum S_i \cdot S_j$ ) yields a good agreement for  $g = 2.078(1)$  and  $J/k_B = -2.85(1)$  K between 6 and 300 K (solid line in Fig. 2). The  $J$ -value obtained from the fit is consistent with the mean-field result,  $|k_B T(\chi_{\text{max}})/JS(S+1)| = 2.53$ , which gave  $|J/k_B| = 2.90$ .<sup>12</sup> Inclusion of a mean-field correction term (*i.e.*,  $zJ'$ ) makes a slight improvement to the quality of the fit, however its value is highly sensitive to the temperature range used.

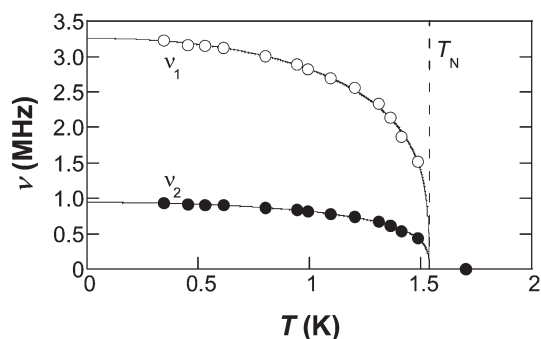
This suggests the interactions between adjacent 2D square nets, which occur *via* the  $\text{HF}_2^-$  bridges, to be very weak, because each  $\text{HF}_2^-$  bridge that connects two  $\text{Cu}^{2+}$  ions lies on the 4-fold rotational axis of the  $\text{Cu } 3d_{x^2-y^2}$  magnetic orbital so that the F  $2p_z$  orbitals cannot overlap with this metal orbital. Nevertheless, spin polarization arguments hint that the  $\text{Cu-F-H-F-Cu}$  pathway may lead to a weak ferromagnetic interaction, *i.e.*  $\text{Cu}(\uparrow)\text{-F}(\downarrow)\text{-H}(\uparrow)\text{-F}(\downarrow)\text{-Cu}(\uparrow)$ , although lower temperature magnetic susceptibility data are needed to confirm this. It should be noted that axial-axial  $\text{Cu}^{2+}$  connections could in turn promote a weak antiferromagnetic interaction as found in  $\text{Cu}(\text{dca})_2(\text{pym})\cdot\text{CH}_3\text{CN}$  for example.<sup>13</sup> While the sign of the exchange interaction along the  $\text{HF}_2^-$  bridge is presently unclear, LRO is expected to occur in  $[\text{Cu}(\text{HF}_2)(\text{pyz})_2]\text{BF}_4$ , albeit likely at low temperature.

In order to search for LRO in  $[\text{Cu}(\text{HF}_2)(\text{pyz})_2]\text{BF}_4$ , we have performed zero-field specific heat and muon-spin relaxation (ZF- $\mu^+\text{SR}$ ) studies. The  $C_p(T)$  measurements were conducted on a Quantum Design PPMS equipped with a 14 T magnet and low temperature insert while a sorption cryostat was utilized on the MuSR spectrometer at the ISIS Pulsed Muon Facility (Didcot, UK).

Specific heat data (Fig. 3) show a broad peak in  $C/T$  near  $\sim 2.5$  K which is likely due to substantial short-range magnetic ordering. Noticeably absent is a  $\lambda$ -anomaly that would signify the onset of LRO. However, close inspection of the data reveals a subtle change in slope around 1.5 K and by plotting  $d(C/T)/dT$  as a function of temperature (Fig. 3, inset), a clear peak is resolved at 1.55 K. Theoretically, it has been found that the magnitude of the  $\lambda$ -anomaly depends on the strength of the 3D magnetic interaction. As the ratio  $J'/J$  approaches 0.01, the  $\lambda$ -anomaly vanishes.<sup>14</sup> This



**Fig. 3** Specific heat for  $[\text{Cu}(\text{HF}_2)(\text{pyz})_2]\text{BF}_4$  obtained at  $H = 0$  plotted as  $C/T$  vs.  $T$  (main) and  $d(C/T)/dT$  vs.  $T$  (inset).



**Fig. 4** Temperature-dependence of the two muon precession frequencies found in  $[\text{Cu}(\text{HF}_2)(\text{pyz})_2]\text{BF}_4$ .

places an upper limit of  $\sim 0.03$  K on the value of  $J'$ , however the susceptibility data suggest that  $J'$  may be even smaller.

Implanted muons act as microscopic magnetometers that can detect small internal magnetic fields in a material.<sup>15</sup> In a magnetically ordered compound below  $T_N$ , the muon spins may precess coherently at a frequency,  $\nu$ , that is proportional to the order parameter of the system. Following this behavior as a function of temperature allows us to probe the magnetic phase transition as shown in Fig. 4. For  $[\text{Cu}(\text{HF}_2)(\text{pyz})_2]\text{BF}_4$ , we find two distinct precession frequencies owing to the presence of two muon stopping sites.<sup>15,16</sup> The lines in Fig. 4 are fits of the data to the power law,  $\nu(T) = \nu(0)[1 - (T/T_N)^\alpha]^\beta$ , where  $\nu_1(0) = 3.26(1)$  MHz,  $\nu_2(0) = 0.94(1)$  MHz,  $T_N = 1.54(1)$  K,  $\alpha = 2.2(1)$ , and  $\beta = 0.29(2)$ . The  $\beta$ -exponent obtained from the fit is similar to the value of 0.326 associated with 3D Ising behavior.<sup>17</sup> Subsequently, the expression,  $\nu_i = \gamma_\mu B_i/2\pi$  ( $\gamma_\mu = 2\pi \times 135.5$  MHz/T), can be used to calculate the corresponding internal fields,  $B_1$  and  $B_2$ , which are 24.1(1) and 7.0(1) mT, respectively. At present we are unable to unambiguously determine the type of magnetic ordering that occurs although we anticipate a collinear antiferromagnetic ordering due to the weak single-ion anisotropy of  $\text{Cu}^{2+}$  and the primary Cu–pyz–Cu exchange pathway that is antiferromagnetic.<sup>16</sup>

To determine whether the  $\text{HF}_2^-$  anion may contribute to the observed LRO, the ratio of  $T_N/J$  can be used as a rough guide. For  $[\text{Cu}(\text{HF}_2)(\text{pyz})_2]\text{BF}_4$ , we obtain  $T_N/J = 0.53$ . This value compares well to those of 0.48, 0.56, and 0.58 calculated for quasi-2D  $\text{Cu}(\text{ClO}_4)_2(\text{pyz})_2$ ,<sup>5c</sup>  $\text{Cu}(\text{C}_5\text{H}_5\text{NO})_6(\text{BF}_4)_2$ ,<sup>18</sup> and  $(5\text{-MAP})_2\text{CuBr}_4$ ,<sup>19</sup> respectively, and is slightly larger than that found for  $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$  (0.42).<sup>20</sup> As the  $T_N/J$  ratio increases, the more significant the 3D magnetic interactions become.<sup>20</sup> Hence, these comparisons seemingly suggest the presence of a non-zero (although weak) exchange interaction along the Cu–F–H–F–Cu pathway. We are currently studying the magnetochemical versatility of this system by substitution of  $\text{BF}_4^-$  for other counter-ions such as  $\text{ClO}_4^-$ ,  $\text{PF}_6^-$ , and others. Additional synthetic and characterization studies are in progress.

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## Notes and references

‡  $\text{NH}_4\text{HF}_2$  (0.2895 g, 5 mmol) and pyrazine (0.7870 g, 10 mmol) are dissolved together in 3 mL of water. To this solution is added, while stirring, a filtered 5-mL aqueous solution containing 1.1860 g (5 mmol) of  $\text{Cu}(\text{BF}_4)_2 \cdot y\text{H}_2\text{O}$ . A dark blue precipitate is obtained immediately. The solid is collected *via* vacuum filtration and dried *in vacuo* for 3 hours. Crystals suitable for structural studies are prepared by a similar method although employing 20-fold diluted solutions. Upon slow solvent evaporation, single crystals are obtained after 2–3 weeks. *NOTE: ammonium bifluoride is highly corrosive and should be handled with care!*

§ Crystal data:  $\text{C}_8\text{H}_9\text{N}_4\text{F}_6\text{BCu}$ ,  $M = 349.54$ , tetragonal,  $a = b = 9.6901(4)$ ,  $c = 6.6193(4)$  Å,  $U = 621.54(5)$  Å<sup>3</sup>,  $T = 298$  K, space group  $P4/mbm$  (no. 125),  $Z = 4$ ,  $\mu(\text{Mo-K}\alpha) = 1.825$  mm<sup>-1</sup>, 5131 reflections measured, 423 unique ( $R_{\text{int}} = 0.0238$ ) which were used in all calculations. The final  $wR(F^2)$  was 0.1220. CCDC 611880. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b608791d

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