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$[Cu(HF_2)_2(pyrazine)]_n$: A Rectangular Antiferromagnetic Lattice with a Spin Exchange Path Made Up of Two Different FHF^- Bridges**

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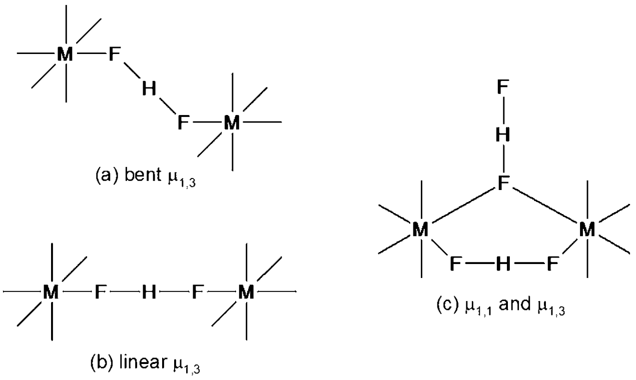
Very little is known about the ligand properties of the bifluoride ion HF_2^- (i.e., FHF^-) in various chemical media including aqueous solution and the solid state. The H⋯F bonds of HF_2^- are the strongest known hydrogen bonds (bond enthalpy of ca. 177 kJ mol^{-1}),[1,2] but the ability of FHF^- to mediate magnetic interactions is not well understood. Various diamagnetic salts of HF_2^- ions have been structurally characterized.[3–8] The only known paramagnetic compounds containing HF_2^- ions are the $[pipzH_2][MnF_4(HF_2)]$ (pipz = piperazine)[9] and $[Cu(HF_2)(pyz)_2]X$ ($X = BF_4^-$,[10] ClO_4^-, PF_6^-,[11] AsF_6^-, SbF_6^-,[12] pyz = pyrazine) coordination polymers.[10–12] $[pipzH_2][MnF_4(HF_2)]$, with angular Mn-FHF-Mn bridges (Scheme 1a), exhibits negligible magnetic coupling, while $[Cu(HF_2)(pyz)_2]X$ with linear bridging $\mu_{1,3}$-HF_2^- ligands (Scheme 1b) shows long-range magnetic order (LRO) between 1.54 and 4.3 K for $X = BF_4^-$ and SbF_6^-, respectively.[10,12] Our efforts to utilize HF_2^- as a synthon much like CN^-, N_3^-, and NCS^-[13–15] have now led to the synthesis of a two-dimensional (2D) rectangular coordination polymer, namely, $[Cu(HF_2)_2(pyz)]_n$, in which the adjacent Cu^{2+} ions are linked by a pyz ligand in one direction, and by two HF_2^- ions with two different bridging modes ($\mu_{1,1}$ and $\mu_{1,3}$ modes, Scheme 1c) in the other direction (Figure 1a). We establish that the $\mu_{1,1}$-mode HF_2^- ion is close in nature to F^-⋯HF, and that the magnetic properties of $[Cu(HF_2)_2(pyz)]_n$ are described by a 2D rectangular antiferromagnetic (AFM) lattice with a weaker spin exchange through the pyz bridge.



Scheme 1. Bridging modes of the bifluoride ion.

The structure of $[Cu(HF_2)_2(pyz)]_n$ was determined by single-crystal X-ray diffraction at 150 K. Each Cu^{2+} ion lies at the inversion center of an axially compressed CuF_4N_2 octahedron with Cu–F1 2.119(3), Cu–F2 2.137(1), and Cu–N 2.003(3) Å (Figure 1a). Very little distortion from ideal octahedral bond angles was observed. Like donor atoms that occupy *trans* positions around the Cu ion (i.e., N-Cu-N, F1-Cu-F1, and F2-Cu-F2) form 180° bond angles. Mirror planes that contain F2, F3, H1, and H2 lie halfway between successive Cu^{2+} ions along the *c* axis and are parallel to the Cu-pyz-Cu chain axis.

Two unique bifluoride bridging modes (Scheme 1c and Figure 1) exist in $[Cu(HF_2)_2(pyz)]_n$, one of which forms a $\mu_{1,3}$-bridge with symmetric H⋯F bonds (H1–F1 1.156(4) Å), where F1⋯H1⋯F1A may be slightly bent (177.4°). The other HF_2^- ion features a unique $\mu_{1,1}$-bridging mode and has asymmetric H⋯F bonds (H2–F3 0.91(3), H2–F2 1.48(3) Å). The H2–F2 bond is only slightly longer than that typically

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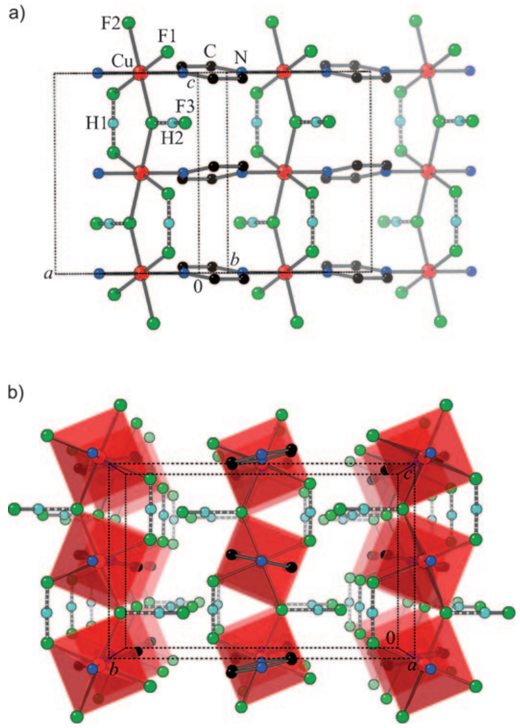

Figure 1. a) Portion of a 2D polymeric sheet and b) *a*-axis view of the layer packing observed in $[Cu(HF_2)_2(pyz)]_n$. The unit cell is shown as dashed lines. Pyrazine H atoms have been omitted for clarity. Dashed cylinders indicate strong H···F hydrogen bonds.

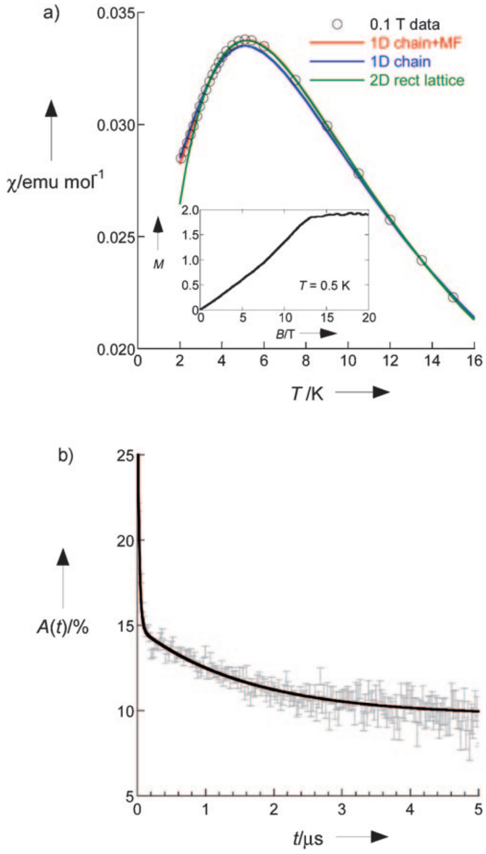

Figure 2. a) Plots of magnetic susceptibility highlighting the low-*T* peak and isothermal magnetization (inset) for polycrystalline $[Cu(HF_2)_2(pyz)]_n$. b) ZF muon-decay asymmetry spectrum measured at 0.02 K. The solid lines in both main plots represent the corresponding theoretical fits as described in the text.

found in asymmetric HF_2^- ions. The possibility of hydrogen-bound H_2O is ruled out because the F···HF bond is shorter than the 1.6 Å typical of F···HOH. Furthermore, IR spectroscopy also revealed no O–H bend (near 1600 cm^{-1}).[16] Hence, the $\mu_{1,1}$-HF_2^- ligand may be more accurately described as an F^-···HF moiety.

Each CuF_4N_2 octahedron in $[Cu(HF_2)_2(pyz)]_n$ is linked to two others through bridging HF_2^- ions along the *c* direction to yield one-dimensional (1D) linear chains (Cu···Cu 3.933(1) Å). These chains are connected by pyz ligands along the *a* axis (Cu···Cu 6.7774(9) Å) to form 2D rectangular sheets (Figure 1b). The sheets pack in registry along the *b* axis, with an interlayer C–H_{pyz}···F1 contact of 2.61 Å. Along the *a* axis, however, the sheets are staggered by one-half of a unit-cell translation to minimize steric interactions between pyrazine H atoms. The neutral $[Cu(HF_2)_2]_n$ chains in $[Cu(HF_2)_2(pyz)]_n$ resemble the motifs found in the 1D polymers $NMe_4[Cu(N_3)_3]$[14a] and $[Cu(N_3)_2(3\text{-}Clpy)_2]$[14b] in that they each have $\mu_{1,1}$ and $\mu_{1,3}$ bridging modes of the N_3^- ligands. The more flexible H···F bonds and variable disposition of the F^- lone pairs in HF_2^- apparently facilitate the formation of planar pentagonal rings in $[Cu(HF_2)_2(pyz)]_n$.

The magnetic properties of $[Cu(HF_2)_2(pyz)]_n$ were explored by SQUID magnetometry, pulsed-field magnetization, and muon-spin relaxation (μ^+SR). A broad maximum in χ versus T (Figure 2a) was observed at 5.2 K, which is indicative of low-dimensional spin correlations, likely within the 2D layers. Below T_{max}, $\chi(T)$ decreases continually as the temperature is lowered and there are no artefacts suggestive of a transition to long-range magnetic order (LRO) above 2 K. The spin correlations between Cu^{2+} ions are antiferromagnetic (AFM), as demonstrated by the temperature-dependence of χT versus T. At 300 K, $\chi(T)T$ has a value of 0.418 emu K mol^{-1}, which exceeds the spin-only value of 0.375 emu K mol^{-1} expected for an isotropic spin-1/2 ion. This discrepancy is attributed to the higher *g* value typically observed for Cu^{2+} ions. Upon cooling, $\chi(T)T$ remains largely invariant until about 50 K, where a rapid decrease ensues to reach a minimum value of 0.057 emu K mol^{-1} at 2 K. The AFM nature of the spin exchange interactions were confirmed by a Curie–Weiss fit of $1/\chi$ versus T ($30 \leq T \leq 300$ K) leading to $g = 2.147(1)$ and $\theta = -2.0(1)$ K.

In each 2D layer of $[Cu(HF_2)_2(pyz)]_n$, the adjacent Cu^{2+} ions are linked by pyz in one direction and by $\mu_{1,1}$- and $\mu_{1,3}$-FHF^- bridges in the orthogonal direction. Thus, the magnetic properties of $[Cu(HF_2)_2(pyz)]_n$ may be described by a spin Hamiltonian $H = -J_{ij}\Sigma S_i S_j$, where J_{ij} refers to the J_{FHF} and J_{pyz} exchanges that define the spin lattice. A least-squares fit of the χ versus T data ($3 \leq T \leq 300$ K) leads to the green curve in Figure 2a and the parameters $C = 0.4269(1)$ emu K mol^{-1}, $J_{FHF}/k_B = -10.099(6)$ K, and $\alpha = J_{pyz}/J_{FHF} = 0.121(1)$ assuming a rectangular lattice model.[17] An equally good fit (red curve) could be achieved for the parameters $C = 0.4185(1)$ emu K mol^{-1}, $J_{FHF}/k_B = -8.13(1)$ K, and $zJ_{pyz}/k_B = -1.80(2)$ K [for $z = 2$, $J_{pyz}/k_B = -0.90(2)$ K, and $\alpha = 0.11(1)$] by using a 1D Heisenberg linear-chain model that included a molecular-field contribution.[18] By comparison, assuming only isolated magnetic chain behavior (i.e., neglecting all possible interchain couplings) the theoretical fit underestimates the experimental curve, as demonstrated by the blue line in Figure 2a. Thus, an additional exchange parameter is needed to fit the data in the vicinity of the maximum.

The inset plot of Figure 2a shows the isothermal magnetization of $[Cu(HF_2)_2(pyz)]_n$ obtained by using a pulsed-field magnet at $T = 0.5$ K. As the field increases, the magnetization rises smoothly but exhibits a concave behavior typical of $S = 1/2$ low-dimensional antiferromagnets.[19] An elbow occurs at a critical field B_c of 12.9 T, and this feature can be used to estimate J_{pyz} on the basis of the principle that $B_c = 2k_B(J_{FHF}+J_{pyz})/g\mu_B$. This expression affords $|J_{pyz}/k_B| = 1.15$ K when $|J_{FHF}/k_B| = 8.13$ K, which is similar to the value obtained from the susceptibility fit. Hence, a 1D model that incorporates substantial interchain coupling seems most appropriate based on the experimental data.

A zero-field (ZF) muon-spin relaxation asymmetry spectrum, measured at 0.02 K is shown in Figure 2b. Across the entire temperature range ($0.02 \leq T \leq 0.9$ K), the spectra display a fast- and a slow-relaxing component described by relaxation rates λ_1 and λ_2, respectively. No oscillation (characteristic of long-range magnetic order) is observed in the muon asymmetry down to as low as 0.02 K. The data are best fitted with a function of the form [Eq. (1)]

$$A(t) = A_1 \exp(-\lambda_1 t) + A_2 \exp(-\lambda_2 t) + A_{bg} \quad (1)$$

where A_{bg} is a constant background offset term, accounting for those muons which stop in the silver sample holder or cryostat tail. At 0.02 K the fitted values in Equation (1) take the values $A_1 = 13\,\%$, $\lambda_1 = 35$ MHz, $A_2 = 5.1\,\%$, and $\lambda_2 = 0.6$ MHz. There is very little variation in the fitted parameters across the measured temperature range. We note that exponential relaxation functions often arise as a result of relaxation due to dynamic fluctuations in the local magnetic field at the muon site.[20] The fact that there is no evidence for long-range magnetic order above 0.02 K implies that the interlayer exchange interactions are extremely weak or there is more disorder in the local field distribution than in related systems that act to suppress the oscillatory response of $A(t)$.

To identify which exchange path—Cu-pyz-Cu or Cu-$(FHF)_2$-Cu—provides the stronger spin exchange and find the relative importance of the $\mu_{1,1}$- and $\mu_{1,3}$-FHF$^-$ bridges in the latter exchange path, we evaluated the Cu-pyz-Cu and Cu-$(FHF)_2$-Cu spin exchanges (designated J_{pyz} and J_{FHF}, respectively, as before) by performing a mapping analysis based on first-principles density functional calculations.[21] Our calculations employed the frozen-core projector augmented wave method encoded in the Vienna ab initio simulation packages,[22] and the generalized-gradient approximation (GGA)[23] with a plane-wave cutoff energy of 400 eV and a set of 32 k-points for the irreducible Brillouin zone. To describe the strong electron correlation in the Cu 3d states, the GGA plus on-site repulsion method (GGA + U)[24] was used with U_{eff} values of 5, 6, and 7 eV.

To extract the values of J_{pyz} and J_{FHF}, we determined the relative energies of three ordered spin states by GGA + U calculations (Figure 3), and then mapped these energies onto the corresponding energies expected from the spin Hamiltonian to obtain $J_{pyz}/J_{FHF} = 0.66$, 0.60, and 0.53 from the GGA + U calculations with $U_{eff} = 5$, 6, and 7 eV, respectively.[25] These ratios are overestimated compared to the ratio $J_{pyz}/J_{FHF} = 0.11$ determined from the analysis of the experimental data. However the qualitative trend, whereby Cu-$(FHF)_2$-Cu is stronger than Cu-pyz-Cu, is consistent.

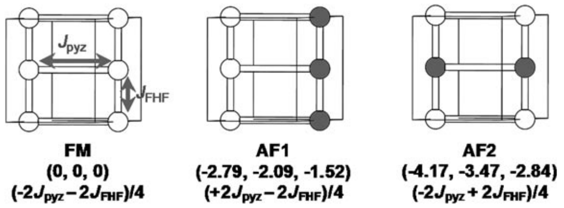

Figure 3. The three ordered spin states of $[Cu(HF_2)_2(pyz)]_n$, with the up-spin and down-spin Cu^{2+} sites represented by empty and filled circles, respectively. The numbers in parentheses, from left to right, are the relative energies in milli electron volts per four formula units (FU), determined from the GGA + U calculations with $U_{eff} = 5$, 6, and 7 eV, respectively. The total spin exchange energy (per 4 FUs) is also given.

To determine the roles of the $\mu_{1,1}$- and $\mu_{1,3}$-bridges in the Cu-$(FHF)_2$-Cu exchange, we examined the spin density plots calculated for the ferromagnetic (FM) and AFM states of $[Cu(HF_2)_2(pyz)]_n$ shown in Figure 4. Clearly, the $\mu_{1,3}$-FHF$^-$ anion contributes mainly its π- and π*-type orbitals to the Cu-$(FHF)_2$-Cu exchange, and hence plays no significant role in the exchange between the two Cu^{2+} ions. The $\mu_{1,1}$-FHF$^-$ anion contributes only the orbitals of the bridging F atom, so that this anion is best described as F$^-$•••H-F, that is, a fluoride anion forming a hydrogen bond with an HF molecule. The s and p orbitals of the bridging F atom make σ-type interactions with the Cu 3d orbitals, so that the $\mu_{1,1}$-FHF$^-$ anion is most important for the Cu-$(FHF)_2$-Cu exchange.

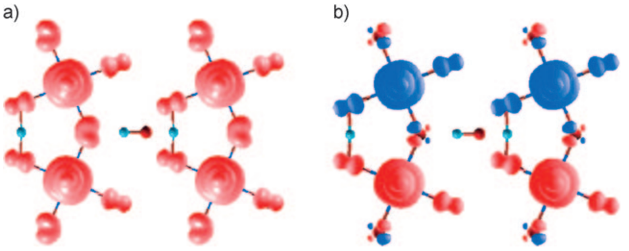

Figure 4. Plots of the spin densities calculated for the a) FM and b) AFM states of $[Cu(HF_2)_2(pyz)]_n$. The view is along the Cu-pyz-Cu axis.

In summary, we have synthesized 2D coordination polymer $[Cu(HF_2)_2(pyz)]_n$, which is well described by a rectangular AFM lattice with $J_{pyz}/J_{FHF} = 0.11$. Our GGA + U calculations show that the weaker spin exchange results from the Cu-pyz-Cu path, and that the $\mu_{1,1}$-FHF$^-$ ion, which is chemically close to F$^-$···HF, is responsible for the Cu-(FHF)$_2$-Cu spin exchange.

Experimental Section

Synthesis: In a typical preparation of $[Cu(HF_2)_2(pyz)]_n$, 10 mL of aqueous HF solution (48 wt %) containing $Cu(CH_3CO_2)_2 \cdot 2H_2O$ (0.3000 g, 1.50 mmol) was mixed with a 10 mL of aqueous HF solution containing NH_4HF_2 (0.0900 g, 1.50 mmol) and pyrazine (0.2410 g, 3.00 mmol) to afford a pale blue solution. Upon standing at room temperature for about 1 month, medium blue rods of $[Cu(HF_2)_2(pyz)]_n$ were obtained in low yield ($<20\,\%$ based on Cu). The material is stable in air for a short period of time but was typically stored in the mother liquor in plastic vials.

Crystal data for $[Cu(HF_2)_2(pyz)]_n$: $C_4H_6CuF_4N_2$; orthorhombic, $Cmcm$, $M_r = 221.65$, $a = 6.7752(3)$, $b = 12.3840(5)$, $c = 7.8908(3)$ Å, $V = 330.42(8)$ Å^3, $Z = 4$, $\rho_{calcd} = 2.224$ g cm^{-3}, $\mu = 3.31$ mm^{-1}, $F(000) = 436$, $R_1 = 0.0407$, $wR_2 = 0.0993$, GOF = 1.170. CCDC 797479 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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