Pressure-Induced Magnetic Crossover Driven by Hydrogen Bonding in CuF$_2$(H$_2$O)$_2$(3-chloropyridine)

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Hydrogen bonding plays a foundational role in the life, earth, and chemical sciences, with its richness and strength depending on the situation. In molecular materials, these interactions determine assembly mechanisms, control superconductivity, and even permit magnetic exchange. In spite of its long-standing importance, exquisite control of hydrogen bonding in molecule-based magnets has only been realized in limited form and remains as one of the major challenges. Here, we report the discovery that pressure can tune the dimensionality of hydrogen bonding networks in CuF$_2$(H$_2$O)$_2$(3-chloropyridine) to induce magnetic switching. Specifically, we reveal how the development of O–H···Cl exchange pathways under compression combined with an enhanced ab-plane hydrogen bonding network yields a three dimensional superexchange web between copper centers that triggers a reversible magnetic crossover. Similar pressure- and strain-driven crossover mechanisms involving coordinated motion of hydrogen bond networks may play out in other quantum magnets.
bond formation to trigger the antiferromagnetic to ferromagnetic crossover in CuF$_2$(H$_2$O)$_2$(3-chloropyridine). Our analysis reveals that compression enhances the in-plane F···H-O exchange and creates new intermolecular hydrogen bonds between chlorine on the pyridine ring and the hydrogen centers on the water ligands. The latter pathway forms because compression reduces interatomic distances, aligns the Cl-containing ring, and widens the H$_2$O ligands, leading to a three-dimensional hydrogen bonding network between copper centers. This increased superexchange network dimensionality drives the 0.8 GPa magnetic crossover. This process is reversible, meaning that when pressure is released, the extra exchange pathway is eliminated. We conclude that magnetic tunability in CuF$_2$(H$_2$O)$_2$(3-chloropyridine) derives from and depends upon the presence of flexible intermolecular hydrogen bonding networks.

Further compression reveals another distortion between 4 and 5.5 GPa involving the bipyramidal copper environment although, at this time, it is not known whether there is a magnetic component. In addition to establishing how pressure-induced changes in bond lengths and angles control magnetism in hydrogen bonded quantum magnets like CuF$_2$(H$_2$O)$_2$(3-chloropyridine), these findings are important for unraveling spin crossover processes and energy transfer mechanisms in other functional materials like multiferroics.

**Results**

Figure 2 (a,c) displays close-up views of the infrared and Raman spectra of CuF$_2$(H$_2$O)$_2$(3-chloropyridine) between ambient pressure and 1.5 GPa. Both sets of spectra show signatures of the 0.8 GPa transition. With increasing pressure, the 125 cm$^{-1}$ infrared active lattice mode diminishes and then disappears. The displacement pattern for this mode is highly collective and involves the F-Cu-F symmetric stretch, the O-Cu-O asymmetric bend, and libration of the 3-chloropyridine ring around the C-Cl bond. Turning to the Raman response, a shoulder around 1575 cm$^{-1}$, which we assign as a combination of C=C and C-N in-phase, in-plane stretches and C-Cl rocking motion, also diminishes and then disappears. Figure 2 (b,d) shows frequency versus pressure plots for these structures. Their disappearance through the 0.8 GPa transition indicates that the lattice is sensitive to the magnetic crossover, a sign of magnetoelastic coupling. Note that we employ room temperature, high pressure data to understand the low temperature response because the spectra are nearly insensitive to temperature. Although the magnetic crossover is observed at low temperatures, our variable temperature measurements show minimal spectral changes down to 4 K (see Supplemental Material), even through the orthorhombic (Pnma) to monoclinic (P2$_1$/c) transition takes place between 200 and 100 K. This allows the use of room temperature, high pressure data to understand the low temperature magnetic crossover.

We carried out lattice dynamics calculations in order to assign the vibrational modes of CuF$_2$(H$_2$O)$_2$(3-chloropyridine) and relaxations to model structural changes between the low-pressure antiferromagnetic and high-pressure ferromagnetic states (Fig. 3 (a–c)) (Schlueter, J. A. Unpublished work). Our calculations predict that the ferromagnetic state becomes energetically favorable above 0.75 GPa, in excellent agreement with the 0.8 GPa crossover found experimentally. As anticipated, most interatomic distances decrease under compression. The drastic decrease in the O-H···Cl distance with pressure is particularly striking. A small discontinuity also appears at the critical pressure. Moreover, one O-H bond length is predicted to increase while the other decreases (such that they become more similar), and the H-O-H bond angle widens dramatically. Taken together, our simulations suggest that changes in the O-H···Cl distance and shape of the H$_2$O ligands are the most important local lattice distortions through the 0.8 GPa transition.

Figure 3 (d–f) displays frequency versus pressure trends for three different vibrational modes: the C-Cl stretches, the H-O-H bend, and the O-H stretches. As our calculations predict, these features are sensitive to the transition. For instance, on approach to the 0.8 GPa transition, the C-Cl stretching modes blue shift with increasing pressure. Above the critical pressure, these same vibrational modes display a much smaller $d\omega/dP$, indicating the stabilization...
of a less compressible phase. At the same time, the H-O-H bond hardens significantly over the entire pressure range, consistent with the prediction of increasing angle\(^{46}\). There is also a notable change in slope through the transition regime. Finally, both O-H stretching features soften under pressure, although at different rates. Softening is characteristic of improved hydrogen bonding interactions\(^{45,57}\), and the divergent rates imply that the two O-H stretching modes in the water ligand are becoming more inequivalent. The latter trend is in apparent contradiction to the aforementioned prediction of one O-H bond shortening and the other shortening. As discussed below, this observation has its origin in the breakdown of simple frequency-bond length correlations\(^{45,64,59}\).

Taken together, we find that hydrogen bonds are established between the H\(_2\)O ligands and the Cl center through the 0.8 GPa magnetic transition (Fig. 1 (b)). The shortened O-H-\(\cdot\cdot\cdot\)Cl distance falls within the range of a “long” hydrogen bond with chlorine\(^{66}\), which explains the hardening of the C-Cl stretching modes as the motion is dampened by the new interaction and increased stability beyond 1 GPa. This interaction also accounts for the disappearance of the 125 cm\(^{-1}\) infrared mode seen in Figure 2 (a), since the O-H-\(\cdot\cdot\cdot\)Cl hydrogen bonds prevent the 3-chloropyridine ring from librating. Since the chlorine center is closer to one hydrogen than the other, the hydrogen bond forces the H-O-H angle to open, dampening the bending motion. This process hardens the H-O-H bending mode. What is formed in the end is essentially an asymmetric pair of O-H bonds (from the point of view of a single H\(_2\)O ligand), in excellent agreement with our calculations (Fig. 3). The establishment of new hydrogen bonding also accounts for the prediction of one O-H bond shortening and the other shortening (Fig. 3(b)). As the hydrogen closer to the chlorine is pulled away from the oxygen center, the bond length of the second O-H linkage ought to be reduced as the electrostatic repulsion is lessened. The intermolecular O-H-\(\cdot\cdot\cdot\)Cl hydrogen bond also shifts the electron density of the oxygen towards chlorine, effectively reducing bond order between the oxygen and the hydrogen center that is not interacting with the chlorine. This is evidenced in our spectra by increased splitting between the two O-H stretching modes as pressure is applied ($-27.5 \pm 2$ vs. $-31 \pm 1$ cm\(^{-1}\)/GPa).

We propose that intermolecular hydrogen bonding between the water ligand and chlorine acts as an additional superexchange pathway between copper centers along the \(c\) axis, adding a third dimension to the hydrogen bonding network in CuF\(_2\)(H\(_2\)O)\(_2\)(3-chloropyridine) above 0.8 GPa (Fig. 1 (b)). Once established, this supplemental linkage, combined with improved in-plane superexchange (due to shorter distances between F centers and H-O-\(\cdot\cdot\cdot\)), facilitates the pressure-induced antiferromagnetic to ferromagnetic crossover. The newly formed O-H-\(\cdot\cdot\cdot\)Cl hydrogen bond decreases the angle of the F-\(\cdot\cdot\cdot\)H-O exchange pathway, making it even further away from the ideal 180° angle to support ferromagnetism. This means that the new hydrogen bond pathway must be the driving mechanism of the magnetic crossover. Since the 0.8 GPa magnetic crossover is driven by these local lattice distortions, the transition should be considered magnetoelastic rather than purely magnetic\(^{46,47}\). Moreover, the crossover is an excellent illustration of how pressure-induced changes in bond lengths and angles modify the transfer integral \(t\) which in turn modifies the exchange interaction \(J\). In this case, the mechanism even changes the sign of \(J\).

While the 0.8 GPa magnetic crossover in CuF\(_2\)(H\(_2\)O)\(_2\)(3-chloropyridine) was previously identified (Schlueter, J. A. Unpublished work), there has been no investigation of structure at higher pressures. We extended our work up to 8 GPa and discovered an additional rather sluggish structural transition between 4 and 5.5 GPa. (Fig. 4) The low frequency Raman spectra are the most revealing in this regard. The appearance of five new modes, along with mode splitting at 120 cm\(^{-1}\) and the disappearance of the 85 cm\(^{-1}\) mode, signal the transition. The infrared-active modes show similar behavior in this pressure range (Supplemental Material). While we cannot precisely assign the new modes that appear, our dynamics calculations show that, in general, modes below 500 cm\(^{-1}\) are related to motion around the copper center, and those above 500 cm\(^{-1}\) are related to the 3-chloropyridine ring. Therefore, we conclude that this higher pressure distortion involves mostly the bipyramidal copper environment, not the 3-chloropyridine ring. The increase in the number of vibrational modes through the transition indicates an overall reduction in symmetry around the copper center. It is clearly a lower symmetry subgroup of \(Pnma\) at 300 K and \(P2_1/c\) below the structural phase transition temperature\(^{41}\). X-ray diffraction will be needed to identify the space group of the high pressure phases.

**Discussion**

Having established the primary role of pressure-induced local lattice distortions in creating new hydrogen bonding pathways which in turn drive the antiferromagnetic to ferromagnetic crossover in CuF\(_2\)(H\(_2\)O)\(_2\)(3-chloropyridine), we turn our attention toward prospects for control. One of the most important criteria in this regard is reversibility. As revealed by Fig. 54, the process is indeed reversible. Hydrogen bond networks form, diminish, and repeatedly reform under pressure. This implies that magnetism, which is determined by the dimensionality of the hydrogen bonding network that provides for superexchange between copper centers, is equally switchable. Whether this process can be demonstrated in thin film form and

![Graph](image-url)
Figure 3 | (a) Relative enthalpy of the CuF$_2$(H$_2$O)$_2$(3-chloropyridine) unit cell, predicting that the ferromagnetic state becomes energetically favored. (b) Calculated H-O bond distances and H-O-H bond angle and (c) H···F and H···Cl distances all indicate sharp changes at the critical pressure. The grey lines indicate the transition pressure which is in excellent agreement with the experimental pressure (0.75 vs. 0.8 GPa). (d) Experimental frequency versus pressure at 300 K for three modes involving the C-Cl bond, (e) H-O-H bend, and (f) O-H stretches. All modes involving the C-Cl bond show slight increases in $d\nu/dP$ around the transition. The H-O-H bend hardens significantly with pressure. The difference in $d\nu/dP$ (27.5 ± 2 vs. 31 ± 1 cm$^{-1}$/GPa) for the two O-H stretches results in increased splitting between the features. Lines are drawn to guide the eye and help visualize different mode behaviors through the transition.

Figure 4 | (a) Raman spectra as a function of pressure. The change in line color denotes a new phase (or coexistence of phases). (b) Raman shift versus pressure over the full pressure range investigated. The critical pressures are marked with grey vertical bands. The orthorhombic to high pressure phase I transition is at 0.8 GPa, and the broad transition with the coexistence of high pressure phases I and II is between 4 and 5.5 GPa. Here, Orth is $Pmna$ orthorhombic (although at low temperature, the material is $P2_1/c$ monoclinic in this regime$^{31}$). HP-I is the first high pressure phase, HP-II is the second high pressure phase, AFM is antiferromagnetic, and FM is ferromagnetic. The magnetic phases are present at low temperature.
under lattice strain is an open question, but similar mechanisms involving coordinated motion of hydrogen bond networks that function as exchange pathways between magnetic centers are likely to play out in other quantum magnets. A secondary criterion is room temperature operation. The O–H⋯Cl connections in CuF₂(H₂O)₂ (3-chloropyridine) are robust at 300 K. However, these connections only function as superexchange linkages at low temperature. We therefore anticipate that pressure- or strain-controllable exchange interactions can be realized only below the ordering temperature, although short range interactions might increase the operating temperature by a few degrees. Materials like V(TCNE)₂·γ(CH₂Cl₂) and (Et₄N)₀.5Mn₁.25[Cr(CN)₆]·2H₂O may offer pressure- and/or strain-driven switchability at high temperatures. Spin–crossover materials may be good candidates as well. Finally, this kind of cooperative functionality is not limited to piezomagnetism. Low power piezo-electric devices may also be possible if magnetoelectric coupling can be made strong enough.

Methods

CuF₂(H₂O)₂(3-chloropyridine) was grown by slowly diffusing a vapor of 3-chloropyridine into an aqueous solution of CuF₂(H₂O)₂(3-chloropyridine), as described previously. Sample quality was confirmed by x-ray diffraction and magnetic susceptibility. A polycrystalline sample was loaded into diamond anvil cells either neat or with a pressure medium (germanium for high and kBr for middle infrared) in order to apply quasi-hydrostatic pressure. The ruby fluorescence technique was used to pressure the sample inside the cell. Raman measurements were performed with a 532 nm diode pumped solid laser, with power below 1 mW to prevent sample degradation. Raman spectra were taken with a resolution of 0.5 cm⁻¹, integrated between 60 and 120 seconds, and averaged three times. Infrared measurements were taken with a resolution of 1 cm⁻¹ for all spectra. Due to the small sample size and 300 μm diamond cuets, the National Synchrotron Light Source at Brookhaven National Laboratory was used for its high brightness infrared light. Standard peak fitting procedures were employed as appropriate. We also measured the variable temperature infrared response at ambient pressure and found no signatures of the orthorhombic to monoclinic transition between 200 and 100 K (Supplemental Material). Thus, we can connect our 300 K, high pressure measurements to the low temperature magnetic crossover. To understand the spectral results as well as the magnetic properties of CuF₂(H₂O)₂(3-chloropyridine), we carried out multi-scale calculations in which both the molecular unit was modeled using molecular orbital theory and the magnetic properties under pressure were calculated via super cell calculations and band structure methods. Using density functional theory with the generalized gradient approximation, we calculated lattice dynamics of a single unit of CuF₂(H₂O)₂(3-chloropyridine) as well as an isolated 3-chloropyridine ring and water molecule to assign the vibrational modes. The relative enthalpy of the antiferromagnetic and ferromagnetic states was calculated at various pressures using spin-polarized density functional theory. See Supplemental Material for additional details.
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Author contributions

J.L.M. conceived the project, developed the plan, and gathered the team. J.A.S. synthesized the material. K.R.O., T.V.B., J.B.W., C.M., Z.L. and J.L.M. performed the spectroscopic measurements. K.R.O. and J.B.W. analyzed the findings and discussed the data with J.L.M., Z.L., T.V.B., S.G., Q.W. and P.J. The theoretical calculations were performed by S.G., Q.W. and P.J. The paper was written by K.R.O., J.L.M. and P.J. with input from all coauthors.

Additional information

Supplementary information accompanies this paper at http://www.nature.com/scientificreports

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