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Magnetic ordering via itinerant ferromagnetism in a metal–organic framework

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Abstract

Materials that combine magnetic order with other desirable physical attributes could find transformative applications in spintronics, quantum sensing, low-density magnets, and gas separations. Among potential multifunctional magnetic materials, metal–organic frameworks in particular bear structures that offer intrinsic porosity, vast chemical and structural programmability, and tunability of electronic properties. Nevertheless, magnetic order within metal–organic frameworks has generally been limited to low temperatures, owing largely to challenges in creating strong magnetic exchange. Here, we employ the phenomenon of itinerant ferromagnetism to realize magnetic ordering at $T_C = 225$ K in a mixed-valence chromium(II/III) triazolate compound, representing the highest ferromagnetic ordering temperature yet observed in a metal–organic framework. The itinerant ferromagnetism proceeds via a double-exchange mechanism, resulting in a barrierless charge transport below T_C and a large negative magnetoresistance of 23% at 5 K. These observations suggest applications for double-exchange-based coordination solids in the emergent fields of magnetoelectrics and spintronics.

The development of multifunctional magnets with optimized magnetic properties in concert with other physical properties such as porosity and high magnetoresistance remains a daunting challenge, with promise to enable new applications in green technologies¹ and next-generation data processing and storage.^{2,3} For realization of commercial applications, it is crucial for a magnet to exhibit a high magnetic ordering temperature beyond potentially elevated operating temperatures. The vast majority of solid-state permanent magnets with high ordering temperatures are based on itinerant magnetism.⁴ In particular, a specific form of itinerant magnetism, known as a double-exchange mechanism, was discovered by Zener in 1951 to explain the coexistence of metallic conductivity and high-temperature ferromagnetism in perovskite mixed-valence manganites, which contain Mn^{III} and Mn^{IV} ions connected by bridging O²⁻ ions.⁵ Here, an itinerant electron is delocalized between e_g orbitals of neighboring Mn ions and consequently promotes a parallel alignment of spins for the localized electrons in t_{2g} orbitals, in accordance with Hund's rules. Many such double-exchange solid-state materials, including cobaltites and Heusler alloys, have since been discovered and investigated for applications in spintronics devices.^{2,6,7}

As an alternative to traditional solid-state materials, metal–organic frameworks, a subclass of coordination solids, are composed of inorganic building units connected by polytopic organic linkers. Compared to solid-state materials, metal–organic frameworks can offer tremendous synthetic versatility for fine-tuning their chemical and physical properties. For instance, organic linkers with predictable binding modes can be utilized to yield frameworks with unique crystal structures and physical properties, which are easily modified through methods including substitution of electron donating/withdrawing substituents on the ligand, post-synthetic redox chemistry, and metal or linker exchange.⁸⁻¹⁰ Furthermore, a combination of a long-range magnetic order and porosity in framework materials could lead to the realization of lightweight permanent

magnets and magnetic separation media.¹¹⁻¹³ Nevertheless, the overwhelming majority of framework materials are not permanent magnets, owing primarily to the inability of diamagnetic organic linkers to mediate the strong magnetic coupling requisite for long-range order. Indeed, only a few strategies have been developed to synthesize coordination solids with high magnetic ordering temperatures, including the employment of short diamagnetic inorganic ligands or organic radical ligands, as exemplified by Prussian blue analogues and the amorphous material V(tetracyanoethylene)₂, respectively.^{11,12,14-18} Alternatively, a potentially powerful, yet unrealized strategy involves the utilization of itinerant charge carriers via a double exchange mechanism. In addition to achieving high ordering temperatures in metal–organic magnets containing diamagnetic linkers, this approach may further provide a means of introducing metallic electronic conductivity.

While double exchange is a recognized phenomenon in solid-state materials,⁵⁻⁷ examples in coordination solids with organic ligands are limited to molecular compounds.^{19,20} Azolate ligands have strong σ -donating and π -accepting abilities, and when coordinated to octahedral metal ions with diffuse d_π orbitals of favorable energies, strong π - d conjugation between ligand and metal orbitals may arise.^{19,20,21} Furthermore, compact, symmetrical azolate ligands can support crystal structures consisting of infinite metal–azolate chains with short metal–metal distances and an octahedral coordination environment around metal ions, providing efficient pathways for long-range charge transport and magnetic interaction.²³⁻²⁵ Herein, we report the mixed-valence framework material Cr(tri)₂(CF₃SO₃)_{0.33}, which exhibits itinerant ferromagnetism with $T_C = 225$ K via a double-exchange mechanism.

Figure 1 Solid-state structures. **a**, Portions of the Cr–N sublattice of the $\text{Cr}(\text{tri})_2(\text{CF}_3\text{SO}_3)_{0.33}$ structure determined from analysis of powder X-ray diffraction data collected at 360 K, showing continuous chromium-triazolate chains forming a diamondoid-type lattice and a disordered, charge-balancing trifluoromethanesulfonate anion in the pore cavity. **b**, A tetrahedral, pentanuclear repeating unit. Purple, yellow, green, red, blue, and grey spheres represent Cr, S, F, O, N, and C atoms, respectively; H atoms are omitted for clarity.

Results and discussion

The compound $\text{Cr}(\text{tri})_2(\text{CF}_3\text{SO}_3)_{0.33}$ is formed through a solvothermal reaction between anhydrous $\text{Cr}(\text{CF}_3\text{SO}_3)_2$ and 1*H*-1,2,3-triazole in *N,N*-dimethylformamide (see Methods and Supplementary Information). The resulting purple solid consists of octahedron-shaped crystals with an edge dimension of $\sim 0.5 \mu\text{m}$ (Supplementary Fig. 1) and is structurally analogous to

reported $M(\text{tri})_2$ ($M = \text{Mg, Mn, Fe, Co, Cu, Zn, Cd}$) materials.^{24,26,27} The material has a diamondoid-type structure formed by corner-sharing tetrahedral pentanuclear repeating units (Fig. 1a), where each unit comprises two crystallographically distinct Cr ions bridged by a 1,2,3-triazolate ligand with Cr1-N1 and Cr2-N2 distances of 2.067(4) and 2.031(6) Å, respectively (Fig. 1b). In addition, the pores of the framework are occupied by disordered CF_3SO_3^- ions. A careful analysis of the refined chemical occupancies reveals the presence of 0.34 CF_3SO_3^- ions per Cr ion, which is close to the expected chemical formula of $\text{Cr}(\text{tri})_2(\text{CF}_3\text{SO}_3)_{0.33}$ if each pore within the framework is filled with a single CF_3SO_3^- ion. The presence of inserted CF_3SO_3^- ions was further confirmed by the low BET surface area of $80 \text{ m}^2 \text{ g}^{-1}$ calculated from an N_2 adsorption isotherm (Supplementary Fig. 3) and elemental analysis for C, H, and N that is consistent with the formula $\text{Cr}(\text{tri})_2(\text{CF}_3\text{SO}_3)_{0.33}$ (see Methods). The presence of charge-balancing CF_3SO_3^- ions in the pores of the framework indicates that the material contains mixed-valence $\text{Cr}^{\text{II/III}}$ centers (see Supplementary Information).

Figure 2 Spectroscopic characterization. **a, b**, Diffuse reflectance UV-vis-NIR (**a**) and infrared (**b**) spectra of $\text{Cr}(\text{tri})_2(\text{CF}_3\text{SO}_3)_{0.33}$ collected at 300 K.

A diffuse reflectance UV-vis-near-IR spectrum of $\text{Cr}(\text{tri})_2(\text{CF}_3\text{SO}_3)_{0.33}$ was obtained to confirm and further probe the mixed-valence electronic structure (Fig. 2a). Notably, the spectrum exhibits an intense absorption band in the near-IR region between 5,000 and 12,000 cm^{-1} , with the absorbance increasing continuously to lower energies. We assign the observed band to an intervalence charge-transfer transition between mixed-valence $\text{Cr}^{\text{II/III}}$ centers. Furthermore, the IR spectrum of $\text{Cr}(\text{tri})_2(\text{CF}_3\text{SO}_3)_{0.33}$ exhibits a broad absorption between 1,500 and 6,000 cm^{-1} , owing to extension of the intervalence charge-transfer transition band into the mid-IR region (Fig. 2b). The absorption band masks most of the expected vibrational modes, leaving few detectable, sharp features. Indeed, absorption bands of similar energies have also been reported for other mixed-valence coordination solids and charge transfer salts.^{21,24,28,29} We note that the presence of such

low-energy transitions suggests a negligible optical band gap stemming from a near-continuous distribution of mid-gap states.

Figure 3 Magnetic properties of $\text{Cr}(\text{tri})_2(\text{CF}_3\text{SO}_3)_{0.33}$. **a**, Variable-temperature zero-field-cooled (open circles) and field-cooled (closed circles) magnetic susceptibility data collected at selected dc magnetic fields of 1000 (red), 100 (green), and 25 Oe (blue). **b**, Variable-temperature out-of-phase ac magnetic susceptibility (χ'') collected with ac oscillating magnetic field of 4 Oe at a frequency of 10 Hz and under zero dc magnetic field. **c**, Variable-field magnetization data collected at selected temperatures with a sweep rate of 33 Oe s^{-1} .

Variable-temperature dc magnetic susceptibility measurements were performed to investigate the magnetic properties of $\text{Cr}(\text{tri})_2(\text{CF}_3\text{SO}_3)_{0.33}$, (Fig. 3a). The plot of magnetization versus temperature features a gradual increase in magnetization upon decreasing the temperature from 350 K, followed by a sudden increase below $\sim 250 \text{ K}$. This sharp rise indicates a magnetic phase transition accompanied by an increased magnetic correlation length within the system. The plot exhibits bifurcation of field-cooled and zero-field-cooled curves below the transition temperature, indicative of spontaneous magnetization. Furthermore, a Curie-Weiss fit to the inverse dc susceptibility data from 300 to 350 K affords $\theta_{\text{CW}} = 268 \text{ K}$, with the positive Curie-Weiss temperature suggesting dominant ferromagnetism, consistent with double exchange (see Supplementary Information and Supplementary Fig. 4a). The presence of magnetic order was confirmed by ac magnetic susceptibility measurements (Supplementary Fig. 4b-f), which show

sharp increases in both the in-phase (χ_M') and the out-of-phase (χ_M'') susceptibilities below 250 K. A precise magnetic ordering temperature was determined as $T_C = 225$ K by locating the temperature at which χ_M'' undergoes a sharp increase from zero. To the best of our knowledge, $\text{Cr}(\text{tri})_2(\text{CF}_3\text{SO}_3)_{0.33}$ exhibits the highest ferromagnetic ordering temperature among all coordination solids and the highest temperature for any type of magnetic order among structurally characterized metal–organic frameworks, with the previous records being $T_C = 107$ K for $[\{\text{Ru}_2(m\text{-fluorobenzoate})_4\}_2(\text{BTDA-TCNQ})]$ (BTDA-TCNQ = bis(1,2,5-thiadiazolo)tetracyanoquinodimethane) and $T_N = 171$ K for $\text{Mn}(\text{TCNE})_{3/2}(\text{I}_3)_{1/2}$ (TCNE = tetracyanoethylene), respectively.^{11,12,30,31} The variable-field magnetization data collected between 3 and 270 K exhibit an S-shaped curve that quickly saturates at a magnetization of $2.39 \mu_B \text{ mol}^{-1}$ at 3 K, close to the expected value of $2.33 \mu_B \text{ mol}^{-1}$ for ferromagnetically coupled low-spin Cr^{II} and Cr^{III} centers present in a 2:1 ratio (Fig. 3c). We note that the presence of mixed-valence low-spin $\text{Cr}^{\text{II/III}}$ ions suggests that the itinerant electrons are housed in the t_{2g} orbitals. The magnetization data do not exhibit a significant hysteresis, with only a small remnant magnetization at all temperatures below T_C , indicating that $\text{Cr}(\text{tri})_2(\text{CF}_3\text{SO}_3)_{0.33}$ is a soft magnet. We note that the cubic crystal structure of the compound, which results in a clear lack of bulk magnetocrystalline anisotropy, is one of the dominant contributors to the observed magnetic behavior with small hysteresis.

Figure 4 Electronic structure calculations and electronic conductivity of $\text{Cr}(\text{tri})_2(\text{CF}_3\text{SO}_3)_{0.33}$. **a,b**, Total **(a)** and projected **(b)** band structure for the ferromagnetic state, calculated using the Perdew-Burke-Ernzerhof (PBE) functional. The zero of energy is set to the highest occupied state. The symmetry points correspond to $\Gamma = (0,0,0)$, $X = (0.5,0,0)$, $Y = (0,0.5,0)$, $Z = (0,0,0.5)$, and $R = (0.5,0.5,0.5)$. **c**, The geometry-optimized structure of $\text{Cr}(\text{tri})_2(\text{CF}_3\text{SO}_3)_{0.33}$. Blue, light blue, brown, and white spheres represent Cr, N, C, and H atoms, respectively; CF_3SO_3^- ion has been omitted for clarity. **d**, Partial density of states (pDOS) in arbitrary units for the ferromagnetic state. The zero of energy is set to the highest occupied state denoted by the dotted vertical line. **e**, Variable-temperature conductivity data of $\text{Cr}(\text{tri})_2(\text{CF}_3\text{SO}_3)_{0.33}$. Blue and red spheres represent measurements taken during cooling and warming, respectively. Green spheres represent data collected while cooling under an applied magnetic field of 7 T. **f**, Magnetoresistance data of $\text{Cr}(\text{tri})_2(\text{CF}_3\text{SO}_3)_{0.33}$ collected at 5 K under selected dc magnetic fields.

Insights into the electronic structure of $\text{Cr}(\text{tri})_2(\text{CF}_3\text{SO}_3)_{0.33}$ were obtained using Density Functional Theory (DFT) (see Supplementary Information for full computational details).

Calculations were performed on the full three-dimensional unit cell, which contains 24 Cr atoms, 48 triazolate ligands, and 8 triflate anions. The results suggest that the ferromagnetic state is lower in energy compared to the antiferromagnetic state by 0.127 eV/Cr atom, in agreement with the magnetic measurements. In the ferromagnetic state, the calculated saturation magnetic moment is $2.41 \mu_B$, which is in excellent agreement with the experimentally measured value of $2.39 \mu_B$. The band structure of $\text{Cr}(\text{tri})_2(\text{CF}_3\text{SO}_3)_{0.33}$ (Fig. 4a) near the Fermi energy predominantly consists of spin-down bands with a large density of states and a band dispersion of ~ 1 eV, suggesting significant spin-polarization. Here, spin polarization is defined as the extent to which the spin is aligned in a particular direction.³² The projected band structure (Fig. 4b) and projected density of states (Fig. 4d) show that both Cr d orbitals and N p orbitals of the triazolate ligands contribute to the valence band maximum and the conduction band minimum. Near the Fermi energy, the frontier orbitals of the bands are dominated by the Cr d_π orbitals and N p orbitals, with approximately 32% hybridization between them, indicating a strong hybridization between the Cr d and N p orbitals and π - d conjugation. Fig. 4d also highlights spin polarization as illustrated by the substantial peak in the spin-down density at the Fermi energy for both the total and the Cr d orbitals. This shows that the Cr d orbitals are primarily contributing to the spin polarized state. The localized charge density (Supplementary Fig. 9) shows alternating high and low charge Cr centers. The Cr centers of lower and higher charges exhibit lower and higher magnetic moments, respectively, consistent with the mixed-valence low-spin $\text{Cr}^{\text{II/III}}$ centers. Notably, the charge density and projected density of states both indicate spin-polarization. Taken together, these computational results demonstrate a ferromagnetic ground state for $\text{Cr}(\text{tri})_2(\text{CF}_3\text{SO}_3)_{0.33}$, and the high density of spin-polarized bands near the Fermi energy arising from a strong π - d hybridization suggests delocalization of electrons

in the valence band maximum, consistent with double exchange stemming from the mixed-valence metal centers.

Variable-temperature conductivity measurements were performed to investigate the charge transport properties associated with double exchange in $\text{Cr(tri)}_2(\text{CF}_3\text{SO}_3)_{0.33}$ (Fig. 4e and Supplementary Fig. 6). Upon cooling from 300 to 200 K, the conductivity decreases very slightly from $\sigma = 1.4(1) \times 10^{-2}$ to $1.3(1) \times 10^{-2} \text{ S cm}^{-1}$. Despite the presence of a slight hysteresis between data measured upon cooling vs warming the sample, the cooling data above 200 K could be fit using the three-dimensional variable-range hopping model (see Supplementary Information). Below T_C and down to 80 K, the compound exhibits a conductivity that is nearly temperature-independent, with $\sigma \approx 1.2(1) \times 10^{-2} \text{ S cm}^{-1}$. An Arrhenius fit to the data in this temperature range yields a small activation energy of 0.14 meV, suggestive of highly delocalized charge carriers. Upon cooling below 80 K, we observed a decrease in conductivity to $\sigma = 4.4(1) \times 10^{-3} \text{ S cm}^{-1}$ at 5 K. The low-temperature data are best fit with the Efros–Shklovskii variable-range hopping model, highlighting a transition back to localized small polarons (see Supplementary Information).³³ Next, conductivity measurements were performed on the same sample pellet while cooling the cell under an applied field of 7 T. Strikingly, the conductivity increases as the temperature is lowered from 225 to 80 K. At 5 K, $\text{Cr(tri)}_2(\text{CF}_3\text{SO}_3)_{0.33}$ exhibits a remarkable maximum negative magnetoresistance of ~23 % (Fig. 4f), representing one of the highest values for any coordination solid.^{34–37} While unprecedented in coordination solids, the observed barrier-less transport behavior in conjunction with the large negative magnetoresistance is consistent with a double exchange mechanism in $\text{Cr(tri)}_2(\text{CF}_3\text{SO}_3)_{0.33}$. The computational results suggest that the partially filled spin-down bands near the Fermi level give rise to a current density that is carried mainly by spin-down charge carriers. Due to the spin-polarized current, the presence of any tunneling junctions

consisting of ferromagnetic domains/layers can yield large magnetoresistance. As $\text{Cr}(\text{tri})_2(\text{CF}_3\text{SO}_3)_{0.33}$ is a soft ferromagnet, the material most likely consists of randomly aligned ferromagnetic domains under zero applied magnetic field. Under an applied magnetic field, the ferromagnetic domains can align parallel to each other, allowing a facile transport of spin-polarized currents. Indeed, large negative magnetoresistance has commonly been observed in solid-state materials with itinerant ferromagnetism.^{38,39}

Conclusions

The foregoing results demonstrate the discovery of itinerant ferromagnetism in a metal–organic framework, which gives rise to an unprecedented magnetic ordering temperature of $T_C = 225$ K and remarkably high magnetoresistance. Importantly, the employed synthetic approach of utilizing π - d conjugation between organic linkers and mixed-valence metal centers with diffuse d_π orbitals provides a general blueprint from which to design materials with enhanced properties, given the vast chemical versatility offered by metal–organic frameworks.

Methods

Synthesis of $\text{Cr}(\text{tri})_2(\text{CF}_3\text{SO}_3)_{0.33}$. All handling of $\text{Cr}(\text{tri})_2(\text{CF}_3\text{SO}_3)_{0.33}$ was performed under a dry N_2 or Ar atmosphere. Liquid 1*H*-1,2,3-triazole (1.04 g, 15.0 mmol) was added to a 20-mL glass scintillation vial containing a solution of $\text{Cr}(\text{CF}_3\text{SO}_3)_2$ (1.75 g, 5.00 mmol) in 10 mL of DMF. The vial was sealed with a polytetrafluoroethylene-lined cap and heated at 120 °C for 3 days. The resulting suspension was cooled to 25 °C and filtered with a Nylon membrane filter to yield a dark purple powder. The powder was washed by soaking in DMF (3×15 mL) and then in dichloromethane (4×15 mL), and was dried under dynamic vacuum (<10 μbar) at 130 °C for 48

h to afford 0.356 g (30%) of product as a purple microcrystalline powder. Anal. Calcd for $\text{CrC}_{4.33}\text{H}_4\text{N}_6\text{FS}_{0.33}\text{O}$: C, 21.91; H, 1.70; N, 35.41. Found: C, 22.24; H, 1.44; N, 35.21.

Magnetic measurements. In a glovebox under an N_2 atmosphere, a sample was prepared by adding an activated powder into a 5-mm-inner-diameter quartz tube containing a raised quartz platform. The sample powder was restrained with a plug of compacted glass wool to prevent crystallite torquing during measurements. The quartz tube was transferred to a Schlenk line and evacuated until the internal pressure reached 30 mTorr. The tube was cooled in liquid N_2 and flame-sealed under static vacuum. All magnetic measurements were performed using a Quantum Design MPMS2 SQUID magnetometer from 3 to 350 K at applied magnetic fields ranging from 0 to ± 7 T. The ac susceptibility measurements were performed with an oscillating field of 4 Oe with a frequency from 1 to 100 Hz. Diamagnetic corrections were applied to the data using Pascal's constants to give $\chi_{\text{D}} = -0.00009744 \text{ emu mol}^{-1}$.

Electrical conductivity measurements. Conductivity measurements were performed using a home-built four-contact cell (Supplementary Fig. 5a). In a glovebox under an Ar atmosphere, a sample pellet was manually pressed in a cell with a known inner cell diameter. While pressed, the cell was sealed with Torr Seal® low-vapor-pressure epoxy. When the epoxy dried completely, the cell was removed from the press for the sample pellet thickness to be measured using a caliper. Room temperature conductivity measurement was performed using a Bio-Logic VMP-3 multipotentiostat fitted to the Ar glovebox. Variable-temperature conductivity measurements were performed in a Quantum Design MPMS2 SQUID magnetometer with a modified sample rod that accommodates ten 26 AWG silver coated copper cables sealed at the top of the rod with an air

tight Swagelock fitting and Torr Seal® low-vapor-pressure epoxy. The airtight sample cell was attached to the SQUID sample rod and inserted into the cryostat-equipped SQUID chamber at 300 K. *I-V* profiles between 5 and 300 K were collected with a Bio-Logic SP200 potentiostat by scanning current between $\pm 50 \mu\text{A}$ and the sample cell allowed to equilibrate for at least 30 min between each measured temperature. All data collected were ohmic within a $\pm 50 \mu\text{A}$ window and were then modelled with Ohm's Law, $E \times \sigma = j$, where E is the applied electric field and j is the current density, to determine the sample conductivity with σ with the units of S cm^{-1} . Magnetoresistance measurements were performed by applying magnetic fields ranging from 0 to ± 7 T during *I-V* profile collections. Data were fitted to charge-transport models as described in the Supplementary Information.

High-resolution powder X-ray diffraction. The powder sample was packed into a 1.0-mm boron-rich glass capillary tube inside a glovebox under an N_2 atmosphere. The capillary was flame-sealed and placed inside a Kapton tube that was sealed on both ends with epoxy. High-resolution synchrotron X-ray powder diffraction data were collected at Beamline 11-BM at the Advanced Photon Source (APS) at Argonne National Laboratory. Diffraction patterns were collected at 360, 220, and 120 K with a wavelength of $0.412685 \text{ \AA}$. Discrete detectors covering an angular range from -6 to 16° in 2θ were scanned over a 34° range of 2θ , with data points collected every 0.001° in 2θ and at scan speed of $0.01^\circ \text{ s}^{-1}$. For all diffraction data from Beamline 11-BM, precise unit-cell dimensions were determined by performing Pawley refinements, after which Rietveld refinements were performed using the software package TOPAS-Academic⁴⁰. High-resolution synchrotron X-ray powder diffraction data between 270 and 5 K (Supplementary Fig. 7a) were

collected at Beamline BM31 at the European Synchrotron Radiation Facility (ESRF) with the wavelength of 0.49754758 Å.

Powder neutron diffraction. Powder neutron diffraction data were collected on the POWGEN instrument at the Spallation Neutron Source (SNS) at Oak Ridge National Laboratory (ORNL). Approximately one gram of sample was loaded into a vanadium POWGEN Automatic Changer can in an He-filled glovebox. Data were collected at the selected temperatures of 300, 150, and 10 K in the high-resolution mode⁴¹.

Data availability

The experimental and computational data that support the findings of this study are available from the corresponding author upon request.

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Author contributions

J.G.P. and J.R.L. formulated the project. J.G.P. synthesized the compound. B.A.C. and J.D.G. performed electronic structure calculations and analyzed data. J.G.P. and L.E.D. collected and analyzed the magnetic data. M.E.Z. collected X-ray absorption spectroscopy data. J.G.P. and M.L.A. collected and analyzed conductivity data. E.V. collected SEM images. H.J. collected and

analyzed the infrared spectra. J.G.P. collected and analyzed powder X-ray diffraction data from APS, with assistance from T.R. M.A.G. collected and analyzed powder X-ray diffraction data from ESRF. M.A.G. and J.G.P. collected and analyzed powder neutron diffraction data. J.G.P. and J.R.L. wrote the paper, and all authors contributed to revising it.

Additional information

The authors declare no competing financial interests. Supplementary information and chemical compound information accompany this paper at www.nature.com/naturechemistry. Reprints and permission information is available online at <http://www.nature.com/reprints/>. Correspondence and requests for materials should be addressed to J.R.L.

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