

Telltale Diamagnetism at 50 K of a Coordination Polymer System

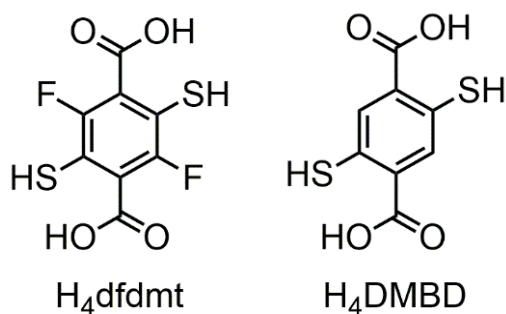
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Abstract: The synthesis of coordination polymers (e.g., Prussian blue) is as old as modern chemistry, but never stops surprising people. Underlying this rich chemistry is the infinite organic molecules that can be designed to link up various metal ions or clusters. We here report superconductivity observed of a designer coordination polymer system sporting the chemically soft mercaptan and hard carboxyl groups. The mercaptan-carboxyl (dubbed Mercarb, or QiuSuo in Mandarin Pinyin) synergy hints at Daoism and here carries over from the molecular to the solid state: the soft sulfur donors bond with $\text{Co}^{2+}/\text{Ni}^{2+}$ (or other transition metal ions) to afford 2D sheets for charge transport, while the interlayer metal-carboxylate domain is more ionic and mediates the transition into the superconductive state. Besides the flexible QiuSuo design, this CP system is open, and allows exchange of molecule guests for tuning the electron-hole balance, in order to achieve high-temperature superconductivity.



Scheme 1 | Molecules H_4dfdmf and H_4DMBD , featuring the mercaptan-carboxyl, or QiuSuo design.

The two major classes of superconductors of cuprates¹ and iron pnictides² both feature covalent charge carrier layers alternating with more ionic layers (e.g., Ln-O) as charge reservoirs. In a formal sense, the chemically soft, polarizable Fe-P or Fe-As layer, in juxtaposition to the chemically hard Ln-O layer, is reminiscent of our long-standing

pursuit in synergizing the soft mercaptan (-SH) with the hard carboxyl functions for coordination network design (as in the dfdmf and DMBD molecules).³⁻⁶ Ideally, to parallel the lamellar character of inorganic superconductors, one would hope for the polarizable metal-thiolate links to enable the charge transport layer, and the ionic metal-carboxylate domain to serve as charge reservoir for modulating the conductive property. However, perhaps due to the proximity of the thiol and carboxyl groups, such spatial and functional division into layered motifs has not been achieved, and the coordination solids had been found to be semiconductive^{3,7} instead of superconductive. Incidentally, in Lu's semiconducting layered structure,⁸ the carboxylate and the thiolate layers appear to be too separate. In general, superconductivity has been observed in coordination networks only at very low temperatures (e.g., 0.25 K).⁹ Here, part with work, part with luck, we have accessed an integrated layered motif in a new class of coordination polymers from the molecules of dfdmf and DMBD, and we are pleased to report the preliminary yet encouraging evidence for their superconductivity behaviors (e.g., with a critical temperature T_c of 50 K achieved already at this opening stage).

The coordination polymers of Ni-dfdmt, Co-dfdmt, CoNi-dfdmt, Co-DMBD and CoNi-DMBD share the formula $\text{Co}_{2-x}\text{Ni}_x(\text{C}_8\text{F}_2\text{S}_2\text{O}_4)(\text{H}_2\text{O})_2$ or $\text{Co}_{2-x}\text{Ni}_x(\text{C}_8\text{H}_2\text{S}_2\text{O}_4)(\text{H}_2\text{O})_2$ ($x = 0, 1$ or 2), and similar crystalline structure (as indicated by powder X-ray diffraction patterns; Figs. 1 and 2).¹⁰ All five were prepared from heating in a sealed glass tube (140 °C) the respective linker

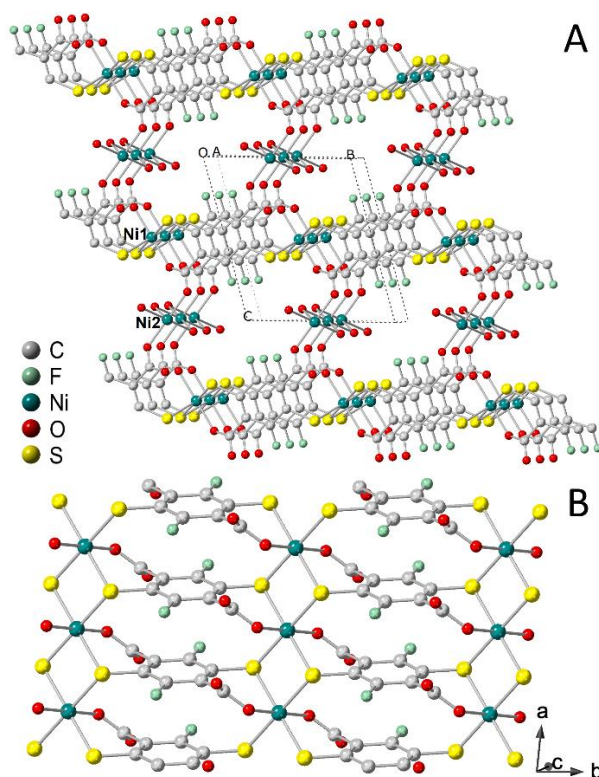


Fig. 1 | Crystal structure of Ni-dfdmt. (A) An overview along the a axis; (B) A 2D Ni-thiolate network viewed along the c axis. H atoms on the aqua sites are omitted for clarity. Grey spheres: C; red: O; cyan: F; yellow: S; green: Ni.

molecule (H_4dfdmt or H_4DMBD) and the metal salts (e.g., $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$), together with water and DMF as the mixed solvent. For illustration, we here describe the crystal structure of Ni-dfdmt (Fig. 1), which has been solved by the MicroED (microcrystal electron diffraction) method (see also SI). Ni-dfdmt is triclinic ($P\bar{1}$; $a = 3.3200$, $b = 8.440$, $c = 9.650$ Å, $\alpha = 74.48$, $\beta = 84.29$, $\gamma = 84.27^\circ$), and features two types of octahedrally coordinated Ni ions (Fig. 1): Ni1 is chelated by the thiol and carboxyl groups, with four equatorial S atoms (Ni-S distances: 2.360 and 2.272 Å) and two apical O atoms (Ni-O distance: 2.008 Å); by sharing two opposite

equatorial edges (i.e., with the μ_2 -S atoms straddling two Ni atoms), straight rows of edge-sharing octahedra is formed along the a axis, and these integrate the benzenoid units into a hybrid metal-thiolate sheet (Fig. 1b). The remaining carboxyl O atoms (these are not coordinated to Ni1) protrude on both sides of the layer and bond to the two apical sites of the Ni2 ion (Ni-O distance:

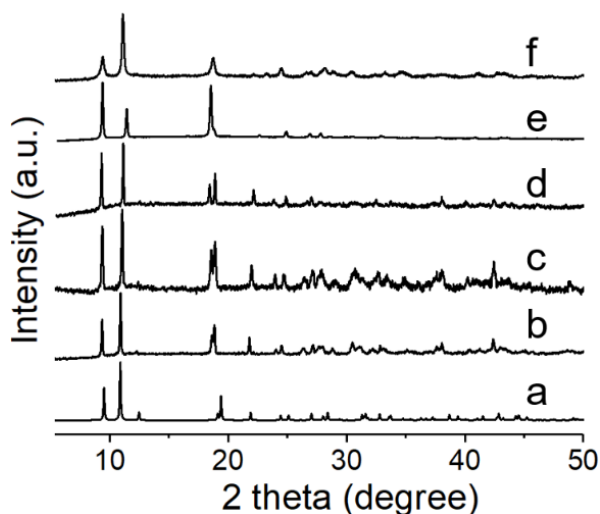


Fig. 2 | PXRD patterns (Cu K α , $\lambda = 1.5418$ Å) of: a) Ni-dfdmt as calculated from the crystal structure; b) Ni-dfdmt; c) Co-dfdmt; d) CoNi-dfdmt, e) Co-DMBD; f) CoNi-DMBD.

1.961 Å). Ni2 is also bonded to four μ_2 -aqua units (Ni-O distances: 2.132 and 2.117 Å), featuring, parallel to the Ni1 chains, rows of edge-sharing octahedra. The Ni2-O chains do not fill up the interlayer space, and small channels (with opening of about 5 Å) exist between the layers. The Ni1-thiolate layer and the Ni2-O domain/interlayer voids thus respectively correspond to the covalent, conducting part and the ionic part in the inorganic superconductors.

The Ni-dfdmt solid has not been found to be superconductive yet, while Co-dfdmt, CoNi-dfdmt, Co-DMBD and CoNi-DMBD all exhibit strong diamagnetism indicative of superconductors. Figure 3 shows their magnetic susceptibilities (χ) as a function of temperature, with those of CoNi-DMBD exhibiting the highest critical temperature (T_c). Under the external magnetic field $H = 5$ Oe (field cooling; FC), the susceptibility starts to decrease at about 55 K and then quickly descends into a value of -0.58 emu g^{-1} at 16 K, followed by slight increase to peak at 7 K. In the zero-field cooling (ZFC) process, the susceptibility starts to decrease slowly at about 60 K, but the sharp descent occurs at a similar temperature (about 50 K) as the FC plot, reaching -0.81 emu g^{-1} at 16 K, followed by slight increase to peak at 7 K. It is not clear yet if this small hump at the cold end is caused by some phase transition or by impurity. A complete shielding (4π

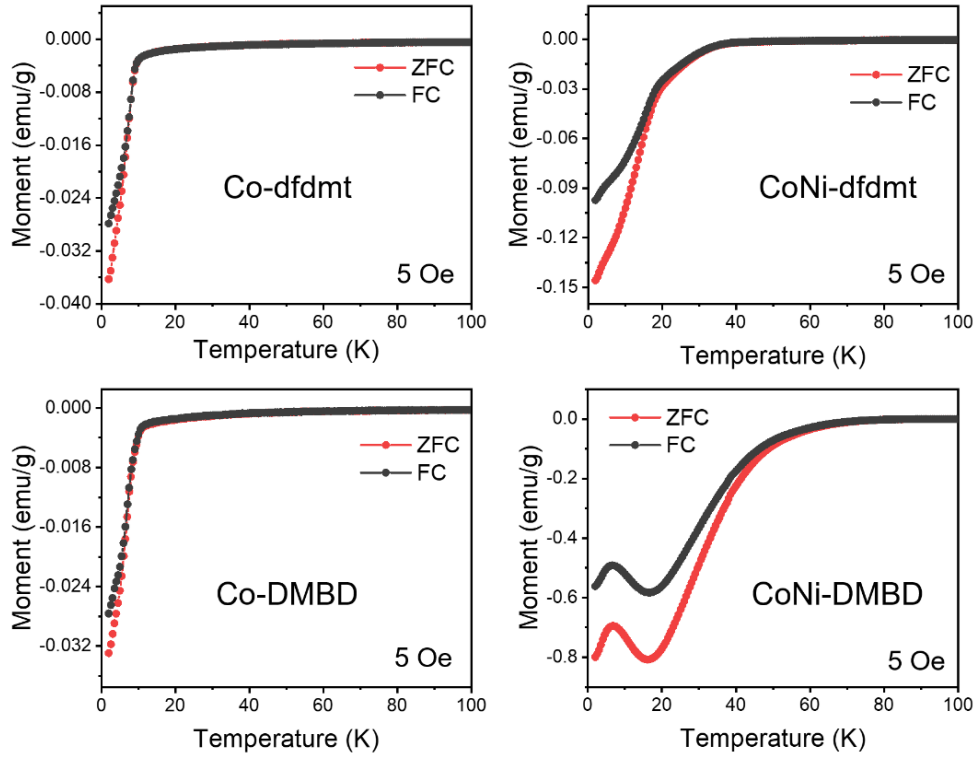


Fig. 3 | Temperature dependence of magnetic susceptibility for the solid samples of Co-dfdmt (14.7 mg), CoNi-dfdmt (11.3 mg), Co-DMBD (9.2 mg) and CoNi-DMBD (10.5 mg). Data are shown for zero-field cooled (ZFC) and field-cooled (FC) measurements at 5 Oe.

$\chi < -1$) is observed, indicating a high-quality superconducting phase. From the inflection point of the χ -T plots, we tentatively ascribe the superconductivity transition temperature (T_c) to be about 50 K for this sample of CoNi-DMBD.

The temperature dependence of the electric resistivity (ρ) of a pressed pellet of the CoNi-DMBD sample was measured by a two-probe setup (Fig. 4). The resistivity exhibits an accelerated growth, reaching an inflection point at about 80 K with a steep upshoot indicative of an emerging insulator state to peak at 55 K, immediately followed by a sharp drop to cross the zero point and stay at the negative region. Is the negative resistivity due to some junction effect? Or is it simply because the resistance of the pellet exceeds the maximum measurable limit of the PPMS

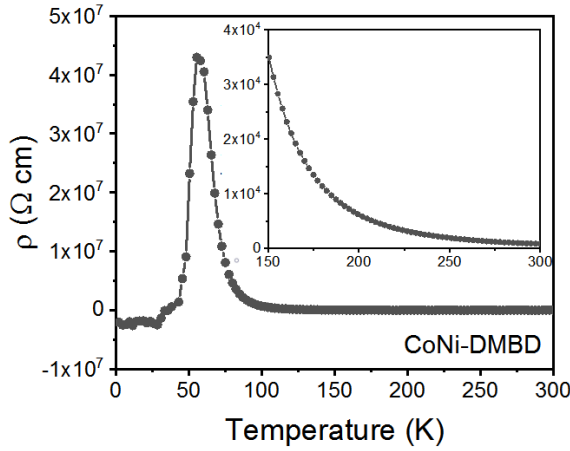


Fig. 4 | Temperature dependence of resistivity of CoNi-DMBD. Resistivity measurements were performed using a two-probe setup. The inset amplifies the 150-300K region

instrument? We are still working for an answer. But the peak resistance temperature thus observed is consistent with the critical temperature T_c value determined from the magnetic susceptibility data (i.e., 50 K); and ongoing, repeated tests on other samples of this series invariably exhibit the same consistency between these two values observed.

Acknowledgments

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Author contributions

J.H. and Z.X. designed and supervised the experiments and measurements. Z.L. and L.T. prepared the coordination polymers. Z.X. saw the link to superconductivity, urged the tests, analyzed the data and wrote the paper. X.Y. measured the magnetic and conductive properties. J.H. and J.Y. also co-edited the paper.

Competing interests: Authors declare no competing interests.

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- 10 A patent based on this study has been filed to the China National Intellectual Property Administration (on Feb. 15, 2022): 202210137451.4.