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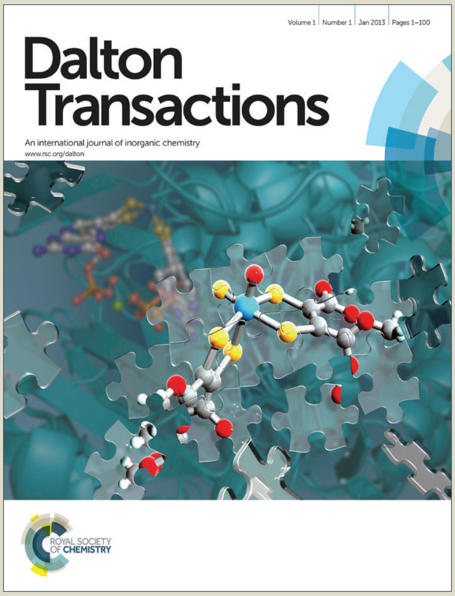

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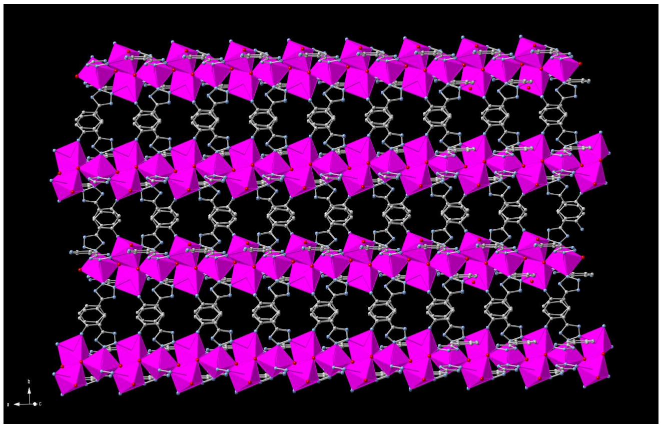
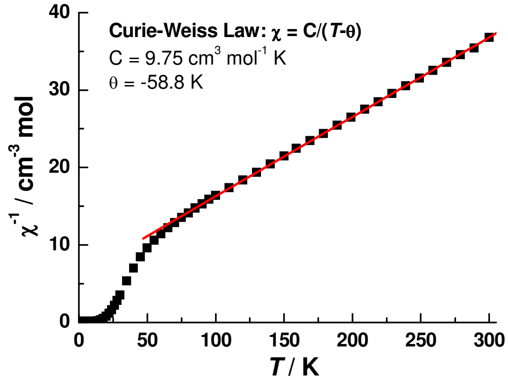
Graphical Abstract

Hydrothermal Synthesis, Structure and Magnetic Properties of a Three-Dimensional Cobalt(II) – Aminophenyltetrazolate Coordination Polymer.

Tiffany M. Smith, Michael Tichenor, Yuan-Zhu Zhang, Kim R. Dunbar, and Jon Zubieta





The three-dimensional [$Co_3(OH)_2(H_2O)_2(aptet)_4$] (aptet = 4-aminophenytetrazolate) exhibits magnetic properties that are consistent with a ferrimagnetic chain with the non-compensating resultant moment of one Co(II) per trinuclear Co(II) subunit and temperature dependence of the ac magnetic susceptibility indicative of glassy-like magnetic behavior.

Hydrothermal Synthesis, Structure and Magnetic Properties of a Three-Dimensional Cobalt(II) – Aminophenyltetrazolate Coordination Polymer.

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Abstract. The hydrothermal reaction of cobalt (II) acetate tetrahydrate, 4-aminophenyl tetrazole and water at 135°C for 48 hours provided blue crystals of $[Co_3(OH)_2(H_2O)_2(aptet)_4]$ (**1**) (aptet = 4-aminophenytetrazolate). The three-dimensional structure of compound **1** is constructed from chains of corner- and edge-sharing Co(II) octahedra linked into a framework through the dipodal ligand tethers. The cobalt sites of the chain are linked through tetrazolate groups in the N2,N3-bridging mode, as well as through μ_3-hydroxyl groups into trinuclear Co_3 substructures. The magnetic properties are consistent with a ferrimagnetic chain with the non-compensating resultant moment of one Co(II) per trinuclear Co(II) subunit. The temperature dependence of the ac magnetic susceptibility indicates glassy-like magnetic behavior.

INTRODUCTION

The contemporary interest in the design of coordination polymers derives from fundamental interest in the targeted synthesis of solid state materials and in the elegant structural chemistry of these materials, as well as their numerous applications to fields as diverse as gas sorption, catalysis and molecular electronics.[1-8] The inorganic substructures of such materials, whether a single metal, metal cluster, or metal oxide building unit, act as nodes, while the organic ligands serve as rigid or flexible multitopic tethers that radiate to adjacent nodes.

While the design of coordination polymers has generally exploited multitopic pyridine and carboxylate ligands as tethers,[9-11] polyazaheteroaromatic ligands, such as imidazole, pyrazole, triazole, tetrazole and their derivatives, have also received considerable attention because of their tendency to bridge multiple metal sites to form polynuclear materials and of their ability to engage in superexchange to provide materials with unusual magnetic properties.[12-27] In addition, polyazaheteroaromatic ligands are readily derivatized to introduce different donor groups and geometric constraints, as reflected, for example, in coordination frameworks exhibiting gas storage properties.[28-32]

In the course of our investigations into the design of coordination polymers, we have characterized a number of materials incorporating triazolate and tetrazolate ligands, as well as their derivatives.[33-48] We noted that the facile derivatization of polyazaheterocyclic ligands allowed the insertion of tethering groups of variable lengths and functionalities, thus providing considerable flexibility in spacer dimensions. The structural influences of tether length were particularly apparent in the series of materials based on triazole and its virtual expanded analogues 4-(4-pyridyl) pyrazolate and 4-pyridyltetrazolate in the N2, N3-bridging modes (Scheme 1). As an obvious extension of this work, the 4-aminophenyltetrazolate ligand was studied as a tether offering expanded spacer distance as well as amine rather than imine coordination at the second terminus of the dipodal tether. The hydrothermal synthesis, structure and magnetic properties of $[Co_3(OH)_2(H_2O)_2(aptet)_4]$ (**1**) are discussed (Haptet = 4-aminophenyltetrazole).

EXPERIMENTAL SECTION

General Considerations

All chemicals were used as obtained without further purification with the exception of 4-aminophenyl tetrazole which was synthesized according to the literature procedure.[49] Cobalt (II) acetate tetrahydrate (99.9%) was purchased from VWR. The synthesis was carried out in a 23-mL poly(tetrafluoroethylene)-lined stainless steel container under autogeneous pressure. The pH of the solution was measured prior to and after heating using pHydrion vivid 1-11® pH paper. Water was distilled above 3.0MΩ in-house using a Barnstead Model 525 Biopure Distilled Water Center.

Synthesis of $[Co_3(H_2O)_2(OH)_2(C_7N_5H_6)_4]$ (Haptet = $C_7N_5H_7$).

A solution of cobalt(II) acetate tetrahydrate (0.20g, 1.1mmol), 4-aminophenyl tetrazole (0.18g, 1.1mmol) and H_2O (10mL, 556mmol) in the mole ratio of 1:1:505 was stirred briefly before heating to 135°C for 48 hours. The initial and final pH values were 6 and 5, respectively. Blue rods suitable for X-ray diffraction were isolated in 35% yield. IR (KBr pellet, cm^{-1}): 3404(s), 3290(s), 3165(s), 3033(s), 2371(m), 1654(w), 1637(w), 1618(s), 1578(w), 1560(w), 1542(w), 1450(s), 1364(m), 1285(w), 1180(m), 1044(m), 830(m), 767(s), 716(m), 624(m), 525(m). Calcd. for $C_{28}H_{30}N_{20}O_4Co_3$: C, 37.9; H, 3.38; N, 31.5. Found: C, 37.7; H, 3.32; N, 31.4.

X-Ray Crystallography

Crystallographic data for $[Co_3(H_2O)_2(OH)_2(C_7N_5H_6)_4]$ was collected on a Bruker KAPPA APEX DUO diffractometer using Mo-K_α radiation (λ = 0.71073Å) containing an APEX II CCD system.[50] The data collection was taken at low temperature (90K). The data were corrected for Lorentz and polarization effects,[51] and adsorption corrections were made using *SADABS*.[52] The structure was solved by direct methods. Refinements for the structure were carried out using the SHELXTL crystallographic software.[53] Following assigning all non-hydrogen atoms, the models were refined against F^2 first using isotropic and then using anisotropic thermal displacement parameters. The hydrogen atoms were introduced in calculated positions and then refined isotropically. Neutral atom scattering coefficients along with anomalous dispersion corrections were taken from the *International Tables*, Vol. C. Images of the crystal structure were generated using CrystalMaker® .[54] Crystallographic details for [$Co_3(H_2O)_2(OH)_2(C_7N_5H_6)_4$] are summarized in **Table 1**.

Thermal Gravimetric Analysis

TGA data were collected on a TA instruments Q500 v6.7 Thermogravimetric Analyzer. Data was collected on a ~5mg sample, ramping the temperature at 10°C/minute between 25°C to 800°C.

RESULTS AND DISCUSSION

Synthesis, Infrared Spectroscopy and Thermal gravimetric Analysis

The title compound was prepared by the hydrothermal reaction of a solution of $Co(CH_3CO_2)_2$•$4H_2O$ and 4-aminophenyl-tetrazole (Haptet) in water. The hydrothermal method is ideal for the preparation of a wide variety of crystalline coordination polymers. In this case, the reaction conditions of 135 ^oC for 48 h under autogenous pressure resulted in the self-assembly of the product from soluble starting materials.[49-54] The hydrothermal method affords a number of advantages when introducing organic components into inorganic structures. These include the reduced viscosity of water under these conditions that enhances diffusion processes, thus favoring extraction of solids and crystal growth, and the minimization of solubility problems that allows introduction of a variety of simple precursors as well as a number of organic and/or inorganic structure-directing agents from which those of appropriate size and shape may be selected for efficient crystal packing during the crystallization process.

The infrared spectrum of [$Co_3(H_2O)_2(OH)_2(aptet)_4$] exhibits several strong bands in the 3000-3400 cm^{-1} range, associated with ν(O-H) of the aqua ligands and the hydroxyl groups. The numerous strong, sharp bands in the 900-1650 cm^{-1} region are attributed to ligand vibrations. The TGA profile of the compound is unexceptional, showing a gradual weight loss of ca. 45% between 320 ^oC and 800 ^oC, most likely reflecting the loss of the coordinated water and partial decomposition of the aminophenyl-tetrazolate ligand to give an oxycobalt-tetrazolate or hydroxycobalt-tetrazolate of the type $Co_xO_y(CHN_4)_z$ or $Co_x(OH)_y(CHN_4)_z$.

Structural Study.

A view of the three-dimensional structure of $[Co_3(OH)_2(H_2O)_2(aptet)_4]$ (**1**) is displayed in **Figure 1(a)**. The structure may be described as one-dimensional chains of Co(II) octahedra linked through aminophenyltetrazolate ligands into a framework. The chains, which propagate parallel to the crystallographic *a*-axis, are constructed from pairs of edge-sharing $\{CoO_3N_3\}$ octahedra linked through corner-sharing $\{CoO_2N_4\}$ octahedra. The metal-oxygen chain substructure exhibits μ_3-OH groups that bridge $\{CoO_3N_3\}$ pairs to $\{CoO_2N_4\}$ sites. Consequently, the shared edge of the $\{CoO_3N_3\}$ pair consists of two hydroxyl ligands, each of which also bonds to a $\{CoO_2N_4\}$ site. Each $\{CoO_3N_3\}$ site is also linked to two adjacent $\{CoO_2N_4\}$ sites through N2,N3-coordinated tetrazolate groups. The coordinated geometry at each $\{CoO_3N_3\}$ site is completed by an amine nitrogen donor from an aminophenyl-tetrazolate group linking a neighboring chain and by an aqua ligand. The $\{CoO_2N_4\}$ sites exhibit *trans*-disposed hydroxyl ligands and nitrogen donors from four tetrazolate groups in the equatorial plane. Each $\{CoO_2N_4\}$ site is thus linked to the four cobalt sites from two adjacent $\{CoO_3N_3\}$ pairs through N2,N3-coordinated tetrazolate groups. The chain substructure of **1** is reminiscent of those observed for the three-dimensional structures of $[Co_3(OH)_2(bime)_2(HO\text{-}BDC)_2]$ (bime = 1,2-bis(imidazole-1-yl) ethane; HO-BDC = 5-hydroxisophthalic acid) and $[Co_3(OH)_2(C_2O_4)_2]$.[61,62] However, the cobalt-oxygen chains of these latter structures exhibit exclusively edge-sharing interactions between the cobalt octahedra.

There are two distinct aminophenyl-tetrazolate ligand environments. The first coordinates to a given cobalt chain through N2,N3-tetrazolate donors and links to an adjacent chain through the amine nitrogen. In this fashion, each cobalt chain is linked to four adjacent chains to establish the three-dimensional connectivity. This pattern produces channels of approximate dimensions 7.70Å by 7.70Å, propagating parallel to the *a*-axis.

The second type of aminophenyl-tetrazolate ligand also coordinates through the N2,N3-tetrazolate donors, but the amino group of the second terminus is pendant. These ligands project into the void channels and exhibit hydrogen bonding between the amine nitrogen and the hydroxyl proton of a neighboring chain ($O_{hydroxyl}\ldots H\text{-}N$: 2.29(2) Å). In addition, the hydrogen atoms of the coordinated aqua ligands act as hydrogen donors toward the uncoordinated nitrogen atoms of the pendant aminophenyl-tetrazolate ligands of an adjacent chain ($N\ldots H\text{-}O$: 1.91(2) and 2.09(2) Å).

The structural chemistry of aminophenyl-tetrazolate complexes remains surprisingly relatively unexplored. Examples incorporating the 4-aminophenyl-1H-tetrazole ligand of this study include the hexanuclear complex $[Re_6S_8(PEt3)_5(aptet)](BF_4)$ [63] and the three-dimensional $[Cd_3(OH)_2(aptet)_4(H_2O)_2]$.[64] The latter material also exhibits two distinct aminophenyl-tetrazolate coordination modes, one through the N2, N3 nitrogen donors of the tetrazolate unit and the amino-group and the second exclusively through the N2, N3 tetrazolate nitrogen donors. There are also several examples of complexes incorporating other positional isomers of aminophenyl-tetrazolate, such as the one-dimensional $[Zn(2\text{-aptet})_2]$ (2-aptet = 2-aminophenyl-1H-tetrazolate) [65] and the three dimensional [Ag(3-aptet)] (3-aptet = 3-aminophenyl-1H-tetrazolate). [66]

Magnetic properties.

Prior to each experiment, the field-dependent magnetization was measured at 300 K in order to detect the presence of any bulk ferromagnetic impurities. For paramagnetic or diamagnetic systems, a perfectly linear line that extrapolates to M = 0 at 0 Oe is expected. The sample measured appeared to be free of any significant extrinsic ferromagnetic impurities. Moreover, from the slope of the *M* vs *H* data at 300 K (Supplementary Figure S4), the estimation for the susceptibility of the compound is 0.027 cm^3/mol (cm^3 = emu/Oe) which compares relatively well with the dc data.

The temperature dependence of the magnetic susceptibility of the compound at 1 kOe is shown in **Figure 2**. At 300 K, the χT product is 8.16 $cm^3 mol^{-1}$ K which is higher than the spin-only value for three S=3/2 ions, indicating the presence of significant orbital contributions for distorted octahedral Co(II) ions.[61] The χT vs. T curve revealed typical ferrimagnetic behavior. Upon lowering of the temperature, the χT product gradually decreases to a minimum of 5.20 $cm^3 mol^{-1}$ K at 55 K, then increases rapidly to a maximum of 79.1 $cm^3 mol^{-1}$ K at 12 K. This behavior is followed by a sharp decrease to 17.4 $cm^3 mol^{-1}$ K at 2 K, attributed to the presence of zero field splitting (ZFS) and antiferromagnetic (*AF*) interchain interactions, which also suggests a long-range ordering below this temperature. The data above 70 K was fit to the Curie-Weiss law ($\chi_M = C/(T-\theta)$) and gives: C = 9.75 $cm^3 mol^{-1}$ K, θ = -58.8 K. The negative θ indicates dominant *AF* coupling between the neighboring Co(II) ions. The structure of the chain, shown in **Figure 3**, indicates that the Co(II) ions (Co2 and Co2A) in the $Co(\mu\text{-}OH)_2Co$ pair are ferromagnetically coupled through the double μ-O bridges due to the small Co-O-Co angles (93.6°), while both are antiferromagnetically coupled to the Co1 ion through the mixed bridges of Co-N-N-Co and the Co-O-Co with angles of 117.41° to 118.48°. As a result, a ferrimagnetic chain is formed with the non-compensating resultant moment of one Co per Co_3 unit. No anisotropic model of this compound could be used to fit the data successfully.

As shown in the inset of **Figure 2**, field-cooled and zero-field cooled magnetization measured in an applied field of 20 Oe indicate bifurcation below *ca.* 10.5 K, suggesting long-range ordering.

The field dependence of the magnetization at 1.90 K is shown in **Figure 4**. The magnetization at higher fields does not saturate, indicating that significant magnetic anisotropy is present. The value (2.64 Nβ) at 70 kOe per Co_3 unit is consistent with the moment of one Co(II) ion, again confirming that the non-compensating resultant moment is from both *F* and *AF* exchange interactions. A considerable, large hysteresis loop with a coercive field of 4 kOe is observed at 1.90 K. The magnetic behavior is reminiscent of that observed for other Co(II) compounds that exhibit ferromagnetic behavior and large coercivities.[61,62,67] **Figure 2** also shows a sharp drop of magnetization at zero and ± 10 kOe.

The ac magnetic susceptibility data collected in the frequency range of 10 – 1490 Hz exhibit a small frequency-dependence in both the real (χ') and imaginary (χ'') parts (**Figure 5**). The best fitting for the relaxation time as determined from the maxima in χ'' leads to unphysical values for U_{eff} of 1203 K $\tau_0 = 2.1 \times 10^{-50}$ sec^{-1}. The rather small value of τ_0, compared with that typically observed for SMMs or SCMs, clearly precludes the possibility of single-chain magnet behavior for **1**. In fact, the shift of peak temperature (T_p) of χ' can be quantified as $\phi = (\Delta T_p/T_p)/\Delta(\log f) = 0.012$, again indicating glassy behavior (where ϕ is around 0.01) rather than a superparamagnet.[68,69]

CONCLUSIONS

The hydrothermal reaction of cobalt(II) acetate tetrahydrate and 4-aminophenyltetrazole yields the three-dimensional coordination polymer, $[Co_3(H_2O)_2(OH)_2(aptet)_4]$. The structure consists of chains of Co(II) octahedra linked through the aminophenyltetrazolate ligands into the framework structure. There are two unique Co(II) sites: pairs of $\{CoO_3N_3\}$ that are linked to

$\{CoO_2N_4\}$ sites through the triply-bridging OH groups. Each cobalt chain is tethered to four adjacent chains through the aminophenyltetrazolate ligands to produce channels that propagate parallel to the *a*-axis that are occupied by the uncoordinated aminophenyl groups of one type of aptet ligand.

The magnetic properties suggest a ferromagnetic chain with the non-compensating resultant moment of one Co(II) per trinuclear Co(II) subunit. The temperature dependence of the ac magnetic susceptibility indicates spin glass behavior, an observation that may require further elucidation.

Supplementary Materials

Tables of atomic positional parameters, bond lengths, bond angles, anisotropic temperature factors, and calculated hydrogen atom positions for $[Co_3(H_2O)_2(OH)_2(C_7N_5H_6)_4]$ in CIF format. ORTEP diagrams for the compound (**Figure S1**). The infrared spectrum, TGA profile, field-dependent magnetization plots and temperature dependence of the inverse susceptibility for $[Co_3(H_2O)_2(OH)_2(C_7N_5H_6)_4]$ are provided in **Figures S2-S5**, respectively.

Material available from the Cambridge Crystallographic Data Centre, CCDC No. CCDC CCDC 986370, comprises the final atomic coordinates for all atoms, thermal parameters, and a complete listing of bond distances and angles, for $[Co_3(H_2O)_2(OH)_2(C_7N_5H_6)_4]$. Copies of this information may be obtained free of charge on application to The Director, 12 Union Road, Cambridge, CB2 2EZ, UK, fax: +44 1223 336 033, e-mail: data_request@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk.

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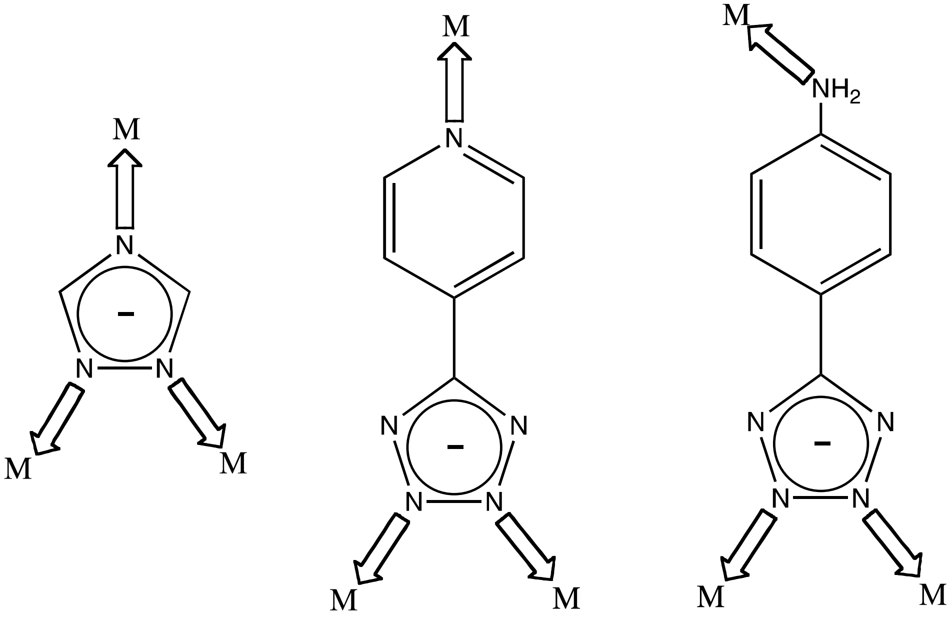
Table 1. Summary of Crystallographic Data for $[Co_3(H_2O)_2(OH)_2(C_7N_5H_6)_4]$.

Empirical Formula	$C_{28}H_{30}Co_3N_{20}O_4$
Formula Weight	887.51
Crystal System	Monoclinic
Space Group	P2(1)/n
a (Å)	6.6673(5)
b (Å)	21.2751(15)
c (Å)	13.0771(9)
α (°)	90
β(°)	102.492(2)
γ(°)	90
$V(Å^3)$	1811.0(2)
Z	2
$D_{calc}(g\ cm^{-3})$	1.628
$\mu\ (mm^{-1})$	1.424
T (K)	90(2)
Wavelength (Å)	0.71073
R_1[a]	0.0232
wR_2[b]	0.0552



Scheme 1

Figure Captions

Figure 1. (a) A mixed polyhedral and ball and stick representation of the structure of $[Co_3(OH)_2(H_2O)_2(aptet)_4]$; (b) a view of the cobalt-tetrazolate chain substructure of $[Co_3(OH)_2(H_2O)_2(aptet)_4]$. Color scheme: Co, purple octahedra; oxygen, red spheres; nitrogen, blue spheres; carbon, black spheres.

Figure 2. Temperature dependence of the χT product for $[Co_3(OH)_2(H_2O)_2(aptet)_4]$ at 1000 Oe. Inset: zero-field cooled magnetization and field cooled magnetization at 20 Oe.

Figure 3. The ferromagnetic chain of $[Co_3(OH)_2(H_2O)_2(aptet)_4]$. The designators *A* in the atom labels indicate that these atoms are located at the equivalent position (2-x, 1-y, 2-z).

Figure 4. *M* vs *H* at 1.9 K for $[Co_3(OH)_2(H_2O)_2(aptet)_4]$. Inset: Hysteresis loops in magnetization at 1.9 K and 5 K.

Figure 5. Temperature dependence of the in-phase (top) and out-of-phase (bottom) components of the ac susceptibility between 10 and 1500 Hz (with 5 Oe of ac modulation) in the range of 2-16 K (left) and 8-14 K (right), measured in zero-dc field. The solid lines are simply guides for visualization.

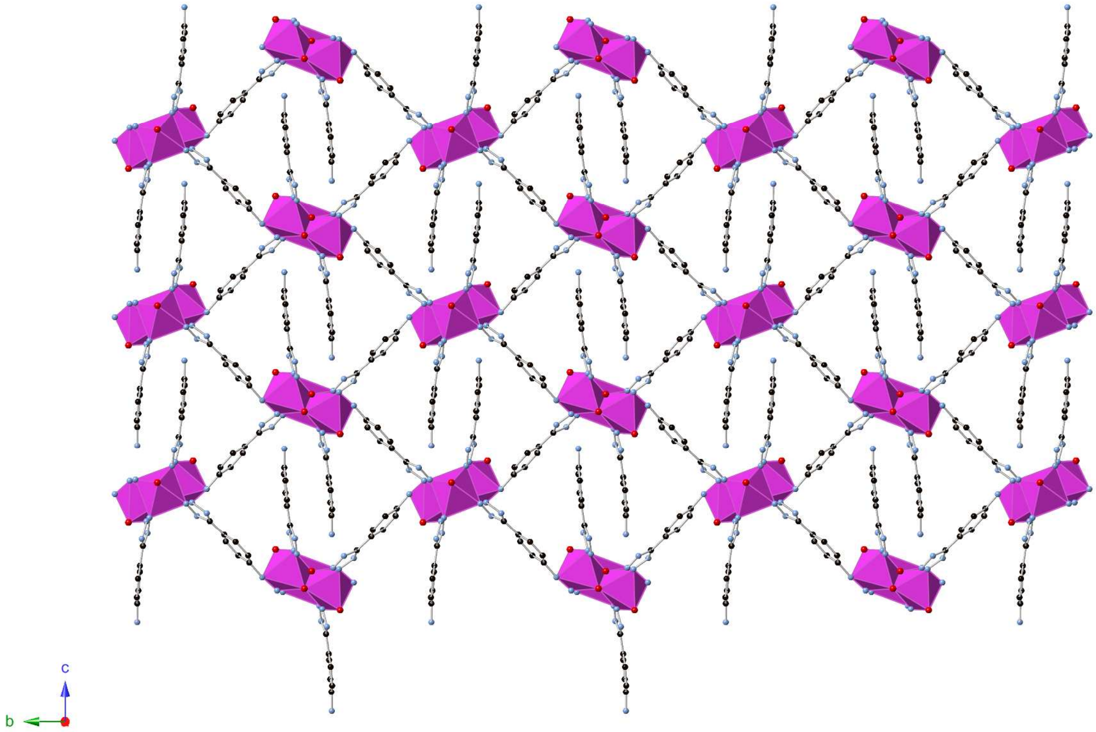


Figure 1a.

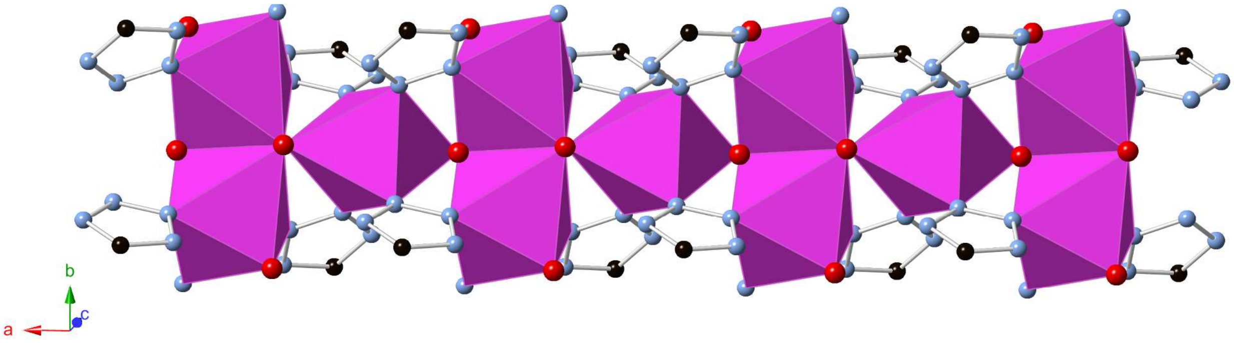


Figure 1b.

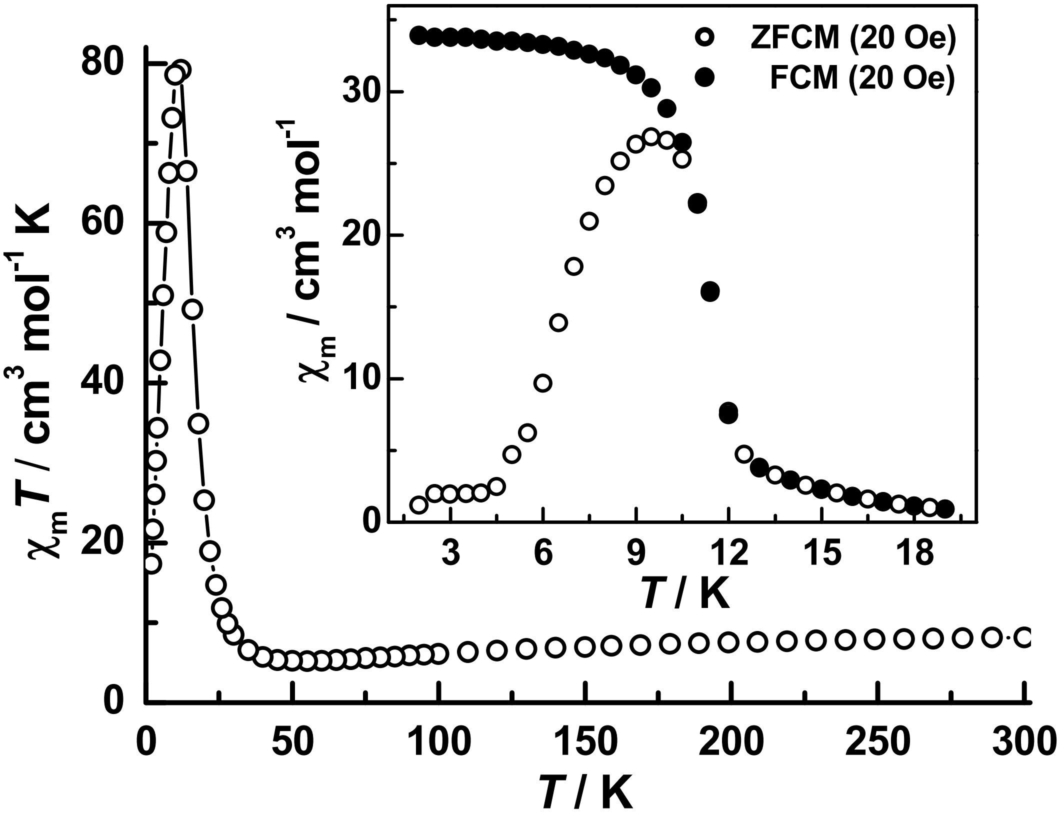


Figure 2.

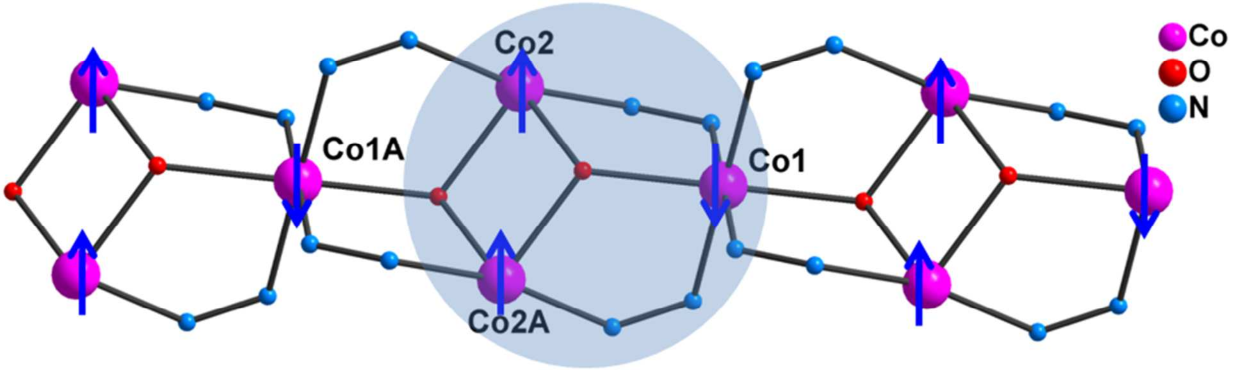


Figure 3.

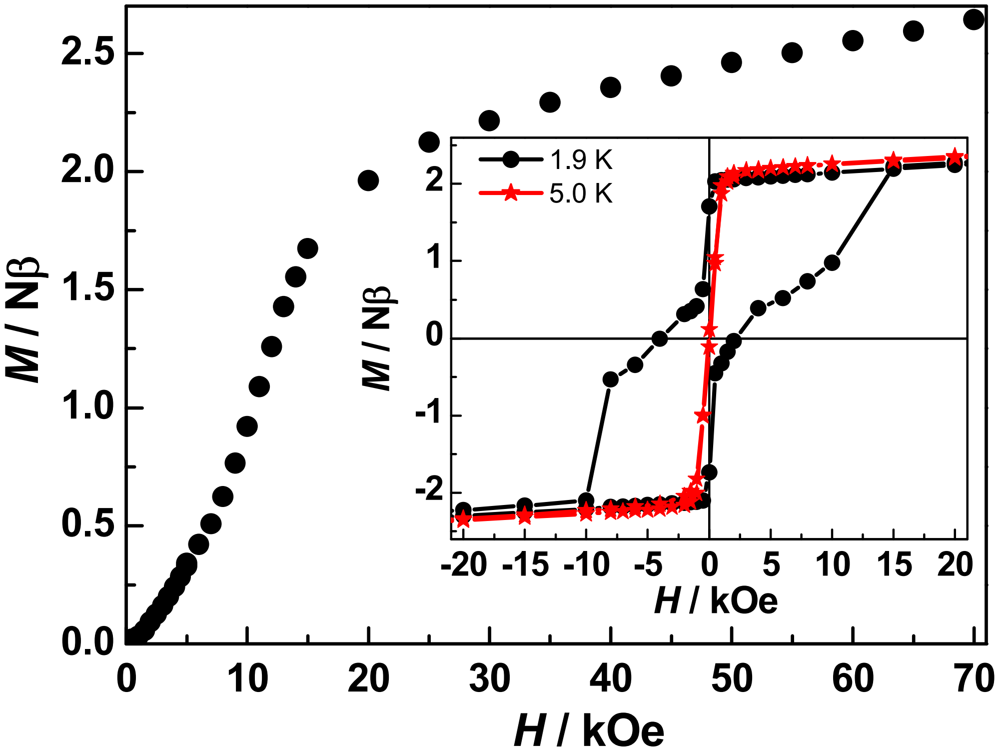
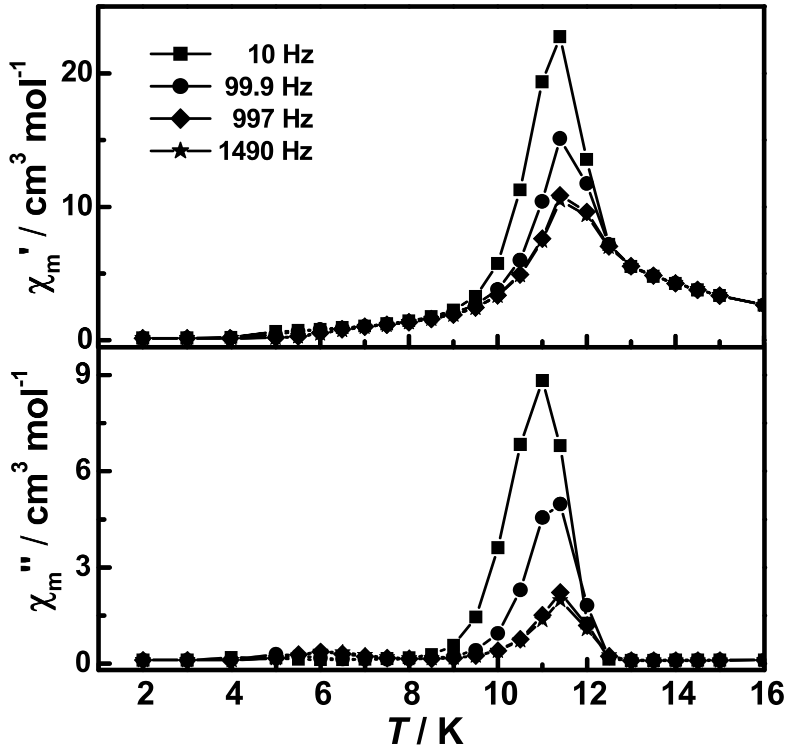


Figure 4.


10 Hz
99.9 Hz
997 Hz
1490 Hz
χ_m' / cm^3 mol^{-1}
0
10
20
χ_m'' / cm^3 mol^{-1}
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3
6
9
2
4
6
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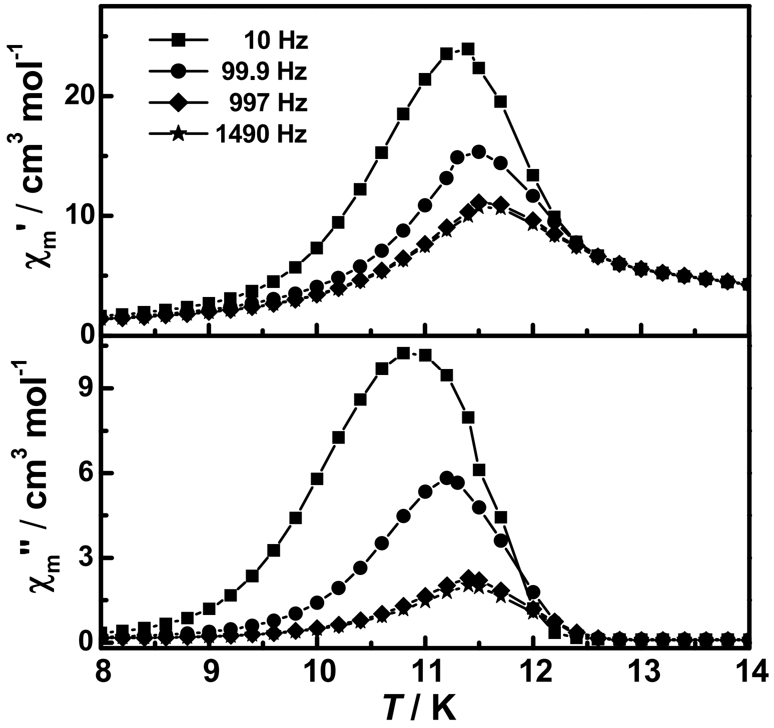
10
12
14
16
T / K


10 Hz
99.9 Hz
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χ_m' / cm^3 mol^{-1}
0
10
20
χ_m'' / cm^3 mol^{-1}
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3
6
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8
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11
12
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14
T / K

Figure 5.