A Simple Synthesis Method for Growing Single Crystals of a Copper Coordination Polymer [Cu(C_2O_4)(4-aminopyridine)_2(H_2O)]_n, and its Theoretical and Physical Properties Studies

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This work reports on a novel and simple synthetic route for the growth of metal–organic crystal [Cu(C_2O_4)(4-aminopyridine)_2(H_2O)]_n of large size using the technique of liquid–liquid diffusion or layer diffusion. Single-crystal X-ray diffraction measurements revealed a very good quality of the grown single crystals with a small value 1.101 of goodness-of-fit R. Rietveld refinement done on powder X-ray diffractogram obtained on few single crystals crushed together revealed a very small value of R as 3.45, indicating very good crystal quality in a batch of crystals. Density functional theory with three different basis sets generated the optimized geometry of a monomeric unit as well as its vibrational spectra. Comparison between experimentally obtained bond lengths, bond angles, IR frequencies, etc. suggests (B3LYP/LanL2DZ, B3LYP/6-311++G(d,p)) basis set to describe the properties the best. Magnetic susceptibility measurements confirm the metal–organic crystal [Cu(C_2O_4)(4-aminopyridine)_2(H_2O)]_n to be a very good representation of a spin 1/2 Heisenberg antiferromagnet.

1. Introduction

Metal–organic coordination polymers are coordination network with organic ligands that link multiple metal centers together, in an infinite array. These polymers have attracted much interest in material science due to their diverse applications in luminescence,[1–3] magnetism,[4–10] gas adsorption,[11–17] and catalysis.[18–21] Low-dimensional magnetism exhibited by such materials is an active research area because of their potential applications as 1D molecular magnetic nanowires and magnetic storage devices.[22] These polymers provide an excellent platform for realizing low-dimensional magnets because of the possibility of tuning both the bridging ligands as well as the co-ligands, thereby, controlling the extent of magnetic exchange interactions and dimensionality.[23] Short bridges such as oxo-, cyano-, or azido-ligands are used as bridging ligands to achieve moderately strong coupling between spin centers.[24–26] An excellent example of a quasi-1D magnet is [Cu(C_2O_4)(4-aminopyridine)_2(H_2O)]_n (abbreviated to 1 henceforth), where oxalate molecules are the bridging ligand that links magnetic centers together, and forms a remarkable physical realization of a spin 1/2 antiferromagnetic Heisenberg chain[27–29] (AfHc), whose excitation spectrum can be investigated using inelastic neutron scattering measurements.

However, since the flux of neutrons in a typical time-of-flight neutron scattering measurement is weak, a large mass and size of the metal–organic crystal is warranted in order to obtain a good signal.[30] Amongst the several approaches to overcome these limitations, the simplest one is to increase the diffraction volume of the crystals.[31,32] Single crystals of the AfHc coordination polymer 1 were first synthesized by Castillo et al.,[27] and later by Prokofiev et al.[28] using the slow diffusion technique. The crystals grown using Castillo’s method were very small that grew as dendrites. Because of their small size, these crystals may not be suitable for neutron scattering experiments. Prokofiev’s technique resulted in large-sized crystals (~1 mm in size). However, the pH of the starting reactants had to be critically controlled, else precipitation of the reactants itself took place. In this paper, we report on a novel and simple synthetic route to grow large-sized single crystals of 1 using the layering technique in which one solution is layered on top of another such that the precipitation process is slowed down, to ensure large-sized crystals. Using this
2. Experimental Section

2.1. Materials and General Methods

All the reagents for synthesis were obtained commercially and used as received; 4-aminopyridine (Merck-Aldrich, 99%), Potassium bis(oxalato)cuprate(II) dihydrate (Merck-Aldrich, 99.999%), Isopropanol (Merck-Aldrich, 99.5%). Fourier transform infrared (FTIR) measurements were done using Shimadzu’s spectrometer (Model No. IRPrestige-21) in the 4000–450 cm$^{-1}$ range using KBr pellet. Thermogravimetric analysis (TGA) and differential scanning calorimetric analysis (DSC) measurements were done in TA Instruments thermal analyzer (Model no. SDT Q600) till 1000 °C at a slow heating rate of 5 °C min$^{-1}$ under nitrogen environment. Magnetization measurements in the temperature range of 1.9 to 300 K were done on a vibrating sample magnetometer mounted on a Physical Property Measurement System from Quantum Design (Model No. Evercool-II). Lower temperature measurements in the range of 0.49 to 2 K were done on a Helium 3 insert attached to Quantum Design’s Superconducting Quantum Interference Device magnetometer (Model iHelium3).

In all the experiments, the crystals were cooled in the zero-field cooling mode to the lowest possible temperature after which a field of 1 T was applied and the data collected in the warming up mode.

2.2. Synthesis

In the present study, crystal growth was based on a binary layering technique (layer diffusion) that involves slow diffusion of one solvent into another resulting in the formation of crystals at the liquid/liquid interface (Figure 1). As mentioned in the introduction, 1 consists of a bridging ligand and a side ligand which were oxalate molecule and 4-aminopyridine, respectively. The source of oxalate molecule was potassium bis(oxalato) cuprate(II) dihydrate. Choosing the most suitable solvent was the main parameter deciding the type, morphology, and structure of the resultant crystal. A solvent in which the potassium bis(oxalato) cuprate(II) dihydrate was moderately soluble was chosen as the first solvent, which in this case, was distilled water. A solvent which was comparatively less dense than the first one and within which 4-aminopyridine was sparingly soluble formed the second solvent, which was isopropanol. Details of the crystal growth were described in the Supporting Information. Dark blue crystals with 65–70% yield (based on copper), as shown in the inset (a) of Figure 1 were obtained. The formed crystals were filtered out and rinsed with a minimal amount of cold distilled water were obtained. The remaining excess solvent was removed by blotting

Figure 1. Cylindrical vessel showing solution A at the bottom and solution B at the top for synthesizing 1 employing liquid–liquid diffusion. Inset a) shows the grown crystals at the liquid–liquid interface Inset b): Images of extracted crystals put on a graph paper for size comparison.

2.3. X-Ray Data Collection and Structure Determination

A tiny crystal was subjected to single-crystal X-ray diffraction (SCXRD) on a Bruker Kappa APEX II CCD diffractometer by the $\omega$ scan technique using graphite monochromatized MoK$_\alpha$ radiation ($\lambda = 0.71073$ Å) at room temperature (293 K). A prismatic crystal with dimensions 0.200 × 0.200 × 0.100 mm$^3$ was carefully selected under a microscope and mounted on a glass fiber. Accurate unit cell parameters and orientation matrix were determined by least-squares treatment of the setting angles of 5402 reflections, of which 1382 reflections were independent, in the $3 \leq 2\theta \leq 26^\circ$ range. The minimum and maximum normalized transmission factors were 0.736 and 0.854. Atomic positions were located by Direct Methods with the structure solution program SHELXT and were then refined by full-matrix least-squares calculations based on $F^2$ using the program SHELXL. All non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were added in idealized geometrical positions. Details of the crystallographic data as well as structural refinement parameters for 1 were given in Table 1. Details of bond lengths, angles, and dihedral angles are given as Supporting Information. The value of goodness-of-fit (GoF) R, 1.101, indicates the quality of the crystals.

2.4. Computational Details

The quantum chemical calculations were done using the DFT method using the Gaussian 16 program package. For calculations of the molecular geometry, atomic coordinates from the crystal structure obtained in Section 2.3, were input into the Gaussian software. Geometry optimization, vibration frequency
Table 1. Crystallographic data of [Cu(C₂O₄)(4-aminopyridine)₂(H₂O)]++.  

| Property | Value |
|----------|-------|
| Empirical formula | C₁₂H₁₄CuN₄O₅ |
| Formula weight | 357.81 |
| Crystal system | Monoclinic |
| Space group | C2 |
| a [Å] | 16.6683(18) |
| b [Å] | 6.3766(7) |
| c [Å] | 6.7632(7) |
| β [deg] | 108.130(3) |
| V [Å³] | 682.19(13) |
| μ calcd [g cm⁻³] | 1.742 |
| Goodness-of-fit on F² | 1.101 |
| Final R indices | R₁ = 0.0177, wR₂ = 0.0440 |
| R indices (all data) | R₁ = 0.0178, wR₂ = 0.0440 |

3. Results and Discussion

3.1. Crystal Structure Details

The crystal structure of 1 consists of Cu²⁺ (spin-1/2) ions, bridged by oxalate molecules (C₂O₄), forming chains along the crystallographic c-axis, as shown in Figure 2a. Aminopyridine and water molecules form side ligands, respectively. The polymer chains lie at a distance of 6.36 Å in the b-direction, as observed in Figure 2b, with the interlayer space being filled by water molecules. The spin chains are well separated (8.32 Å) and magnetically screened by nonmagnetic amino-pyridine groups along the a-axis. The screening of the Cu²⁺ spins by water molecules along the b-direction and amino-pyridine groups along the a-direction makes it a quasi-1D system along the c-axis. Copper has a coordination of a square pyramid with Cu lying within the basal plane formed by oxygen atoms of two oxalate ligands and the nitrogen atoms of two 4-aminopyridine ligands. The bond distances are 2.006 and 1.998 Å for the basal Cu—O and Cu—N bonds, respectively. The basal plane of the square pyramidal structure is parallel to the ac plane. The apical Cu—O bond (2.290 Å) connects the copper atom with the oxygen of the water molecule.²⁷,²⁸

Figure 2c shows the geometry of the oxalate ligand that acts as a bridge between two neighboring copper ions. The oxalate ligand is not planar and the two CO₂ entities (O2-C6-O1 and O4-C7-O3) are twisted ±28° with respect to each other around the C6—C7 bond. The values of the dihedral angles (O1-C6-C7-O3) and (O2-C6-C7-O4) are 28.4° and 27.4°, respectively. The distance between the two oxygen atoms O6 and O8 is 2.788 Å. The oxalate binds the copper ions only through two oxygen atoms belonging to the two carboxylate moieties (O6, O8) of the oxalate. The remaining two oxygen atoms are free and do not bind to the copper ions. This situation is very rare and is usually not found where typically both the oxygen atoms of the oxalate molecules bind to the metal ions.³⁹,⁴⁰ The free oxygen atoms of the carboxylate moieties (O7, O2) make an extensive network of hydrogen bonds with water molecules shown as dashed lines in Figure 2b,c.

The coordination sphere of copper(II) governs the electronic structure of the 3d³ Cu(II) ion and the nature of the orbital describing the unpaired electron (“magnetic orbital”). From the short metal-ligands distances (around 2 Å), it can be deduced that the magnetic orbital is of the dₓ²−ᵧ² type with x roughly along O6-CuO1 and y along N2-CuN4.⁴¹ A schematic representation of the exchange pathway mediated between the two neighboring copper ions through the oxygen atoms of the bridging oxalate molecule is shown in Figure 2d. The twist of the oxalate ligand can be clearly seen in Figure 2d. The twist decreases the overlap of magnetic orbitals and can partly explain the low value of the coupling constant J_k Bern in 1.

The asymmetric unit of 1 consists of a Cu atom attached to a 4-aminopyridine molecule, three oxygen atoms, one carbon atom, and one hydrogen atom as shown in Figure 3a. The simplest unit obtained by optimizing the geometry of 1 that is generated by using the DFT i) B3LYP/6-311G++(d,p) basis set, ii) B3LYP/LanL2DZ basis set, and iii) an ONIOM model with LanL2DZ for the Cu atom (metal center) and 6-311G++(d,p) for the rest of the atoms (organic part). The charge and spin multiplicity in all quantum chemical computations were taken as 0 (neutral) and 2 (doublet), respectively. The computed vibrational modes, obtained using Gaussview 6 program, have been used for the molecular structural and vibrational analysis. The calculations converged to an optimized geometry since there were only real harmonic vibrational wavenumbers, revealing the localization of energy minima. Harmonic infrared vibrational wavenumbers were calculated for the fully optimized molecular geometry. The differences between calculations and experiments were accounted for by scaling the generated vibrational frequencies using standard scaling factor 0.9679.

3.2. Exchange Pathway

The exchange pathway is generated using the three basis sets (i), (ii), and (iii) described above are shown in Figure 4a–c, respectively. The structure of the 3d³ Cu(II) ion and the nature of the orbital describing the unpaired electron (“magnetic orbital”). From the short metal-ligands distances (around 2 Å), it can be deduced that the magnetic orbital is of the dₓ²−ᵧ² type with x roughly along O6-CuO1 and y along N2-CuN4. A schematic representation of the exchange pathway mediated between the two neighboring copper ions through the oxygen atoms of the bridging oxalate molecule is shown in Figure 2d. The twist of the oxalate ligand can be clearly seen in Figure 2d. The twist decreases the overlap of magnetic orbitals and can partly explain the low value of the coupling constant J_k Bern in 1.

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Figure 2. Crystal structure of 1: a) shows the structure in the a–c plane while b) shows the structure in the b–c plane; c) shows the geometry of the oxalate ligand. d) Schematic representation of magnetic interaction via $d_{x^2-y^2}$ orbital of Cu(II) ions and $p_x$ orbitals of the oxygen atoms of the bridging oxalate ligands.

Figure 3. a) Asymmetric unit generated from single-crystal XRD. Simplest unit generated from density functional theory using basis sets b) (B3LYP/6-311++ G(d,p)), c) (B3LYP/LanL2DZ), and d) (B3LYP/6-311++ G(d,p), B3LYP/LanL2DZ).

Table 2. Experimental and calculated (B3LYP/LanL2DZ, B3LYP/6-311++ G(d,p)) geometrical parameters of $[\text{Cu(C}_2\text{O}_4)(\text{4-aminopyridine})_2\text{H}_2\text{O}]_n$.

| Parameters          | Experimental | Calculated (B3LYP/LanL2DZ, B3LYP/6-311++ G(d,p)) |
|---------------------|--------------|-----------------------------------------------|
| Bond length [Å] Cu-N2 | 1.99833      | 2.02479                                       |
| Cu-N4               | 1.9983       | 2.02490                                       |
| Bond angle [°] Cu-N2-C5 | 122.7800    | 121.9885                                      |
| Cu-N2-C1            | 120.3642     | 120.3060                                      |
| Cu-N4-C12           | 122.7799     | 122.9341                                      |
| Cu-N4-C8            | 120.3641     | 119.5413                                      |
| Cu-O6-C13           | 116.8008     | 108.9527                                      |
| H6-O5-Cu            | 122.1022     | 101.4099                                      |
| Dihedral Angle [°] Cu-N2-C5-H5 | 2.3260   | 5.9726                                        |
| Cu-N2-C1-H1         | 2.9925       | 6.8271                                        |
| Cu-N4-C12-C11       | 177.0        | 177.5867                                      |
| Cu-N4-C8-C9         | 177.7        | 177.8909                                      |
| Cu-N4-C12-H12       | 3.0          | 2.0565                                        |
| Cu-N4-C8-H8         | 2.3          | 0.7873                                        |

be found in the Supporting Information. It is to be observed that the bond lengths as well as the bond angles have an agreement with the experimental values, given the fact that the calculations have been done on a single isolated molecule in the gaseous state.
Figure 4. Monomeric unit of 1 generated using density functional theory using basis sets a) (B3LYP/6-311++G(d,p)), b) (B3LYP/LanL2DZ), and c) (B3LYP/6-311++G(d,p), B3LYP/LanL2DZ).

Figure 5. Rietveld fit of [Cu(C\(_2\)O\(_4\))(4-aminopyridine)\(_2\)(H\(_2\)O)]\(_n\) powder where red filled circles indicate the observed data, black solid line is the fit, blue line is the difference curve and black bars indicate Bragg positions corresponding to the [Cu(C\(_2\)O\(_4\))(4-aminopyridine)\(_2\)(H\(_2\)O)]\(_n\) phase.

while the experimental values correspond to molecules in the solid state.

3.2. Rietveld Refinement

To ensure that no competing co-crystallizing phases grow using this new technique or phases within 1 grow that are hard to detect in an SCXRD, we resorted to Rietveld refinement of 1.

Red filled circles in Figure 5 represent the data points obtained in a powder diffractogram that was obtained by crushing few single crystals of 1 and grinding them together for 10 min to make a powder. The grinding time of 10 min was chosen to ensure that a homogeneous powder with sufficient number of random grains necessary for diffraction is obtained. Details of the calculations are provided in the Supporting Information. Black solid line is a Rietveld fit that was obtained using the JANA software.[42,43]

Table 3 summarizes the obtained parameters of the fit, while Table 4 describes the fractional coordinates of all the atoms, the Debye–Waller factor, \(U_{iso}\), as well as occupancies of each atom. The GoF is obtained by minimizing the weighted sum of the squared difference between the observed and calculated values of the intensity using the least square method, and obtained as 3.45. The difference curve plotted as blue curve in Figure 5, shows a small finite value only for few peaks (for most peaks it is negligible) due to intensity mismatch at such positions that may arise due to conformal changes in pyridine or oxalate molecule which were not refined. The small value of GoF was obtained without having to incorporate any preferred orientation function, intergrowth phases, or co-crystallizing phases. One can conclude from the SCXRD measurements that our growth technique affords good single crystals and from the Rietveld analysis that there are no competing intergrowth or co-crystallizing phases.

3.3. Thermal Analysis

To check the thermal stability of the grown crystals, TGA measurements, as shown in Figure 6, were done. Figure 6 shows a thermogram of 1 collected in the temperature range from room temperature up to 1000 °C. Red solid line represents the TGA measurement while the blue dotted line shows the DSC measurement done simultaneously to determine the nature of the underlying change (endothermic or exothermic). The weight change in 1 is seen to happen in two steps. In the first step, a shallow peak is observed in the TGA curve at 177 °C accompanied by an endothermic peak in the corresponding DSC curve, which suggests that the shallow peak at 177 °C corresponds to a weight loss which was found to be 5.5% of the total weight. This weight loss is attributed to the loss of water whose calculated value is 5.05%. A unique characteristic of [Cu(C\(_2\)O\(_4\))(4-aminopyridine)\(_2\)(H\(_2\)O)]\(_n\) is that the crystal undergoes a distinct color change from deep blue to pale blue.
Table 3. Various parameters of Rietveld refinement obtained on \([\text{Cu}(\text{C}_2\text{O}_4)(4\text{-aminopyridine})_2\text{(H}_2\text{O})]_n\) using JANA software.

| Lattice constants | \(a\) | \(b\) | \(c\) | \(\alpha\) | \(\beta\) | \(\gamma\) |
|-------------------|--------|--------|--------|--------|--------|--------|
|                   | 16.64891 | 6.363616 | 6.755812 | 90     | 108.1083 | 90     |

Profile parameters

|                  | \(U\) | \(V\) | \(W\) | \(L_x\) | \(L_y\) |
|------------------|-------|-------|-------|--------|--------|
|                  | 83.03542 | –82.97326 | 43.26922 | 6.271958 | 1.87654 |

Zero correction: 1.03964

Asymmetry correction

| Method correction | \(H_pS\) \(L^{-1}\) | \(H_mS\) \(L^{-1}\) |
|-------------------|---------------------|---------------------|
| by divergence     | 0.000219            | 0                   |

Space group: C2 (Unique axis b)

Background correction: Manual

Agreement factors: GoF 3.45

Table 4. Fractional coordinates, \(U_{iso}\), and site occupancy for \([\text{Cu}(\text{C}_2\text{O}_4)(4\text{-aminopyridine})_2\text{(H}_2\text{O})]_n\).

| Atom type | Label | \(x\) | \(y\) | \(z\) | \(U_{iso}\) | Occ |
|-----------|-------|-------|-------|-------|-------------|-----|
| C         | C1    | 0.660880 | 0.731900 | 0.579100 | 0.0247859 | 1   |
| H         | H1    | 0.626599 | 0.830738 | 0.491159 | 0.03       | 1   |
| C         | C2    | 0.745130 | 0.776000 | 0.661100 | 0.0243561 | 1   |
| H         | H2    | 0.766453 | 0.902879 | 0.631209 | 0.029      | 1   |
| C         | C3    | 0.799110 | 0.628300 | 0.790500 | 0.0213696 | 1   |
| C         | C4    | 0.761350 | 0.445900 | 0.835300 | 0.0242     | 1   |
| H         | H3    | 0.793883 | 0.345008 | 0.924115 | 0.029      | 1   |
| C         | C5    | 0.675460 | 0.416400 | 0.747200 | 0.0251783 | 1   |
| H         | H4    | 0.651580 | 0.294171 | 0.779113 | 0.03       | 1   |
| C         | C6    | 0.496410 | 0.681100 | 0.112500 | 0.0173652 | 1   |
| N         | N1    | 0.524740 | 0.555100 | 0.617800 | 0.0219131 | 1   |
| N         | N2    | 0.882820 | 0.661900 | 0.870100 | 0.0293756 | 1   |
| O         | O1    | 0.510980 | 0.511000 | 0.212900 | 0.0200682 | 1   |
| O         | O2    | 0.477290 | 0.849100 | 0.177400 | 0.0286705 | 1   |
| O         | O3    | 0.500000 | 0.155000 | 0.500000 | 0.0335521 | 0.5 |
| Cu        | Cu1   | 0.500000 | 0.514630 | 0.500000 | 0.0167034 | 0.5 |
| H         | H5    | 0.918900 | 0.556000 | 0.953000 | 0.042      | 1   |
| H         | H6    | 0.904800 | 0.789000 | 0.835000 | 0.019      | 1   |
| H         | H7    | 0.487000 | 0.077000 | 0.377000 | 0.12       | 1   |

during dehydration which is reflected in the water loss in the TGA spectrum. After the shallow peak at 177 °C, a sharp peak in the TGA curve accompanied by a sizeable endothermic peak is observed at 199 °C. The sharp peak corresponds to ≈68% of weight loss in the coordination polymer. This weight loss may arise due to loss of gases like CO_2 arising from the disintegration of oxalate and 4-aminopyridine. The sharp endothermic peak shows that except for the liberation of crystalline water at 177 °C, this crystal is stable up to 199 °C without any phase transition.

3.4. FTIR Analysis

Figure 7a shows the experimentally obtained FTIR spectrum of 1 at room temperature while the FTIR spectra generated using the three bases sets described above are shown in Figure 7b–d, respectively. From the room temperature FTIR spectra of Figure 7a, we assigned the main IR features (\(\text{cm}^{-1}\), KBr pellet), \(\nu = 1655\) (s;
Figure 7. a) Experimental FTIR spectra of 1 at room temperature. FTIR spectra of 1 generated from DFT calculations using basis sets as b) (B3LYP/6311G++(d,p)), c) (B3LYP/LanL2DZ), and d) (B3LYP/LanL2DZ, B3LYP/6-311++G(d,p)).

Figure 8. FTIR spectra of 1: a) as-synthesized, b) heated at 220 °C, and c) heated at 650 °C.

Figure 9. Thermal dependence of molar susceptibility, $\chi_M$, of 1 represented by red circles in a) temperature range of 300–0.49 K and b) lower temperature range of 0.49–4.2 K. Black solid curve in each is a fit to the Bonner–Fisher expression 2. See text for details.

3.5. Magnetic Properties

The temperature-dependent magnetic susceptibility of 1 measured at an applied field of 1 Tesla is shown in Figure 9. For the analysis, single crystals of the total mass of 0.975 mg were co-aligned and mounted on the sample holder with vacuum grease. Filled red circles in the main panel of Figure 9 show the magnetic susceptibility of the title compound in the entire temperature range from 300 K up to the lowest measured temperature of 0.49 K. As seen from Figure 9a, the magnetic susceptibility increases with decreasing temperatures and passes through a maximum value at $\approx 1.9$ K. The presence of a low-temperature maximum is a clear indication of the existence of quasi-1D antiferromagnetic exchange interactions governed by the Hamiltonian, Equation 1:

$$H = \sum_{i=1}^{n-1} \vec{S}_i \cdot \vec{S}_{i+1}$$

where $\vec{S}_i$ represents the spin on the ith magnetic ion, namely, Cu, and the summation is over all nearest neighboring copper spins. Antiferromagnetic interaction between copper ions along the chain arises due to the overlap between two neighboring...
magnetic d$^{2,2,2}$ orbital of Cu(II) ions resulting in delocalization of spin density on the bridging oxalate ligand.

The black continuous curve in Figure 9 is a fit to the expression

$$\chi (T) = \chi_0 + \chi_1 + \chi_{\text{BI}} (T)$$ (2)

where $\chi_0$ is a small positive constant to account for uncoupled spins; $\chi_1$ corresponds to the diamagnetic contributions from closed atomic shells of the title compound, estimated from Pascal’s table$^{[45]}$ and $\chi_{\text{BI}} (T)$ is the magnetic susceptibility estimated from the Bonner–Fisher model$^{[46]}$

$$\chi = \frac{N g^2 \mu_B^2}{k_B T} \left( 0.25 + 0.074795 x + 0.075235 x^2 \right)$$

where symbols have their usual meaning and $x = J/k_B T$. From the fits, $\chi_0$ and $\chi_1$ were obtained as $4.44 \times 10^{-5}$ and $-107 \times 10^{-6}$, respectively. Reduced chi-square C, defined as $C = (1/DOF) \sum (\chi_{\text{calc}}(i) - \chi_{\text{exp}}(i))^2$, where DOF is the degree of freedom, was found to be $2.74 \times 10^{-4}$. An attempt to fit the data with any possible interchain coupling constant $J' k_B^{-1}$ in the meanfield approximation resulted in an order of magnitude small values, and hence, was neglected. So, the GoF between the theoretical expressions 2, 3, and the experimental data, points to the fact that the title compound is a very good representation of a spin 1/2 Heisenberg antiferromagnetic chain, with negligibly small interchain coupling constant $J'$, in agreement to other reports.$^{[27,28]}$

The slight difference between the experimental data and that arising from the theoretical fit at low temperatures may be due to the fact that the Bonner–Fisher model calculates the susceptibility of a spin $\frac{1}{2}$ AFHc considering only 11 spins while the experimental data is for a very large number of atoms. From the fit, an intra-chain coupling $J/k_B \approx (3.16 \pm 0.06)$ K was obtained, in exact agreement with the value obtained from$^{[27]}$ (2.2 cm$^{-1} = 3.16$ K). The obtained value of $g$ is 2.27.

4. Conclusion

In conclusion, we have successfully synthesized large-sized (of length ≈1 mm) single crystals of a copper coordination polymer [Cu(C$_2$O$_4$)(4-aminopyridine)$_2$(H$_2$O)$_n$] via a novel and simple growth technique compared to the existing techniques of crystal growth of this compound. Crystals, grown through liquid/liquid or layer diffusion technique, were characterized by different experimental techniques. DFT with different basis sets was employed to generate the asymmetric unit of the polymer, bond lengths, etc. and compared with experimentally obtained data. Magnetic susceptibility measurements reveal the compound to be an extremely good representation of a spin 1/2 Heisenberg chain. The largeness of the crystals makes them an attractive candidate for neutron scattering experiments.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

The authors thank M. Padmanabhan for his help and support in the initial stages of the synthesis of the crystals.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

density functional theory, liquid/liquid diffusion, low-dimensional magnets, metal–organic crystals

Received: June 20, 2020
Revised: October 15, 2020
Published online: January 14, 2021

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