



Synthesis, structure and magnetic properties of copper(II) complexes of 2-amino-5-trifluoromethylpyridine (5-TFMAP): (5-TFMAP)₂CuX₂ (X = Cl or Br), (5-TFMAP)₃CuBr₂ and [(5-TFMAP)₂CuBr₂](5-TFMAPH)Br



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ABSTRACT

Reaction of 2-amino-5-trifluoromethylpyridine (5-TFMAP) with copper halides in water or alcohol solvents produced four coordination complexes: (5-TFMAP)₂CuX₂, (X = Cl (**1**) or Br (**2**)), (5-TFMAP)₃CuBr₂ (**3**) and [(5-TFMAP)₂CuBr₂](5-TFMAPH)Br (**4**). In all compounds, the 5-TFMAP ligands are coordinated to the Cu(II) ion through the pyridine nitrogen atom in a *trans*-geometry and a nearly square planar environment is observed in **1**, **2** and **4**. In **3**, coordination of an additional 5-TFMAP ligand results in a distorted trigonal bipyramidal complex. All complexes are characterized by single-crystal X-ray diffraction. Compound **1** crystallizes as a chain structure via pairs of long Cl...Cu contacts between molecules and the temperature dependent magnetic susceptibility data has been fit to an alternating chain model, resulting in $J = -5.97(1)$ K and $J' = -0.95(4)$ K. Compound **2** exhibits weaker antiferromagnetic interactions, also via the bihalide superexchange pathway, resulting in $J = -3.02(2)$ K from a fit to the uniform chain model. The structure of compound **3** also exhibits a uniform antiferromagnetic chain, but via the two-halide pathway (short Br...Br contacts) and susceptibility data exhibit significantly stronger interactions ($J = -31.05(5)$ K). Compound **4** is not stable in air and loses a molecule of 5-TFMAP from the crystal lattice upon standing.

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1. Introduction

The synthesis and characterization of complexes of the general formula L₂CuX₂ and (LH)₂CuX₄ (where L is an organic ligand/base, LH is the protonated base, and X is either Cl or Br) is highly relevant to the expansion of inorganic chemistry and theoretical physics with respect to understanding the nature of magnetic interactions. The study of quantum antiferromagnets (AFM) is extremely important for the continued understanding of magnetic exchange theory. When studying low-dimensional quantum Heisenberg antiferromagnets (QHAF), the magnetic behavior is known to depend on the superexchange pathways and those superexchange pathways are dependent on the structure of the compound [1]. The characteristics of the Cu(II) ion, with a single unpaired electron and a g-factor of approximately 2.00, in a coordination complex allows for observations into the field of quantum magnetism [2]. The

relative positions of the Cu(II) ions within the crystal lattice is determined by the number and nature of the ligand and ancillary species in the compound and the nature of the superexchange pathways they may provide. Variation of the steric and electronic properties of the ligands alters the structure of the complex which in turn modifies the superexchange pathways and therefore the magnetic behavior of the material. These alterations in structure can form lattices comprising chains, dimers, honeycombs, ladders, layers, and three dimensional systems [3–8].

In our studies of such compounds, we have examined a wide variety of organic ligands to observe how the modification of substituents on those ligands affects the crystal lattice and magnetic superexchange. We have focused on copper(II) halide complexes and copper(II) halide salts in which the halide ion is either chloride or bromide. It has directed us into studying the behavior and characteristics of the 2-amino-5-substituted-pyridine (5-SAPH) family of compounds. Data on this family is known for 2-amino-5-methylpyridinium and 2-amino-5-chloropyridinium CuX₄²⁻ salts (X = Cl, Br) and for the 2-amino-5-bromopyridinium tetrabromocuprate salt where two-dimensional magnetic layers were formed [9].

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Related compounds where S=H [10], CN [11], NO₂ [12], F [13], and I [14] have also been reported which generate a wide variety of lattice types.

In the two-dimensional layer compounds, it was observed that the bulkiest substituent (Me) resulted in longer halide...halide contact distances and, accordingly, weaker magnetic exchange in the copper(II) complex [9]. We were interested in how these properties might vary by substituting a trifluoromethyl substituent for the methyl group. The trifluoromethyl group has been used as an isosteric replacement for halogen atoms and, in spite of the somewhat longer C–F bond compared to the C–H bond, as an isosteric replacement for a CH₃ substituent [15]. Although the steric properties of 2-amino-5-trifluoromethylpyridine (5-TFMAP) may be similar to those of 5-MAP, the electronic nature of the two compounds are vastly different considering the polarity difference between the C–H and C–F bonds. This electronic difference provides an opportunity to further investigate how the electronic structure of the molecule alters the final compound. We have previously reported the synthesis, structure and magnetic properties of the chloride and bromide tetrahalocuprate salts of 5-TFMAP which occurred as a magnetic ladder (chloride, $J_{\text{rung}} = -13.9(1)$ K and $J_{\text{rail}} = -2.9(4)$ K) and a honeycomb-like lattice (bromide, $J \sim -1$ K) [16] unlike the corresponding 5-MAP compounds where both the chloride and bromide salts crystallized as two-dimensional square magnetic lattices. A hydroxy-bridged Cu(II) dimer with 5-TFMAP has also been characterized both in structure and magnetism [17].

Intrigued by the significant structural changes induced by introduction of the CF₃ substituent, as well as the resulting change in magnetic behavior, we have attempted the synthesis of the corresponding neutral compounds, (5-TFMAP)₂CuX₂ (X is Cl or Br). The synthesis, structure, and magnetic properties of these complexes, along with the unanticipated isolation of (5-TFMAP)₃CuBr₂ and the co-crystal (5-TFMAP)₂CuBr₂·(5-TFMAP)Br are reported.

2. Experimental

Copper(II) bromide was purchased from Sigma–Aldrich, propan-1-ol was purchased from Alfa Aesar and 2-amino-5-trifluoromethylpyridine (5-TFMAP) was purchased from Matrix Scientific. All materials were used without further purification. Copper(II) chloride dihydrate was purchased from Specialty Chemicals Division and was heated at 180 °C for 48 h to obtain the anhydrous compound.

2.1. Synthesis of bis(2-amino-5-(trifluoromethyl)pyridine)dichloridocopper(II) (1)

A solution of anhydrous copper(II) chloride (0.804 g, 1.5 mmol) in 15 mL of propan-1-ol was added slowly with stirring to a solution of 5-TFMAP (0.500 g, 3.08 mmol) in 15 mL of propan-1-ol resulting in a dark greenish-yellow solution which was left covered with parafilm for slow evaporation at room temperature. Dark green crystals formed at the bottom of the beaker after 6 days, which were recovered by vacuum filtration, washed with 2-methylpropan-2-ol and allowed to air dry to yield 0.1102 g (16% yield). IR (KBr, ν in cm⁻¹): 3414 (m), 3326 (m) 3219 (w), 1657 (w), 1640 (m), 1572 (w), 1525 (w), 1425 (w), 1363 (w), 1331 (s), 1283 (w), 1194 (w), 1151 (w), 1112 (s), 1083 (m), 918 (w), 828 (w), 752 (w), 636 (w). CHN Calc. for C₁₂H₁₀N₄F₆Cl₂Cu: C, 31.42; H, 2.20; N, 12.21. Found: C, 31.4; H, 2.10; N, 11.85%.

2.2. Synthesis of bis(2-amino-5-(trifluoromethyl)pyridine)dibromidocopper(II) (2)

A solution of copper(II) bromide (0.140 g, 0.658 mmol) in 15 mL of water was added slowly with stirring to a solution of 5-TFMAP

(0.161 g, 1.00 mmol) in 15 mL of water resulting in an aqua-colored solution. Within minutes, the solution became turbid. It was left to slowly evaporate. The solution was gravity filtered every other day over the course of one week to remove traces of a light blue precipitate which was shown by IR and powder X-ray diffraction to be copper(II) hydroxide. When the solution had evaporated completely, dark brown crystals had formed. The product was recrystallized with hot methanol. The resulting dark brown crystals were washed with 2-methylpropan-2-ol and allowed to air dry to yield 0.4755 g (86.83% yield). IR (KBr, ν in cm⁻¹): 3413 (m), 3323 (m), 3217 (w), 1674 (w), 1640 (s), 1567 (m), 1520 (w), 1420 (w), 1325 (s), 1282 (w), 1184 (m), 1119 (m), 1080 (m), 915 (w), 856 (w). CHN Calc. for C₁₂H₁₀N₄F₆CuBr₂: C, 26.32; H, 1.84; N, 12.21. Found: C, 26.7; H, 1.72; N, 11.7%.

2.3. Synthesis of tris(2-amino-5-(trifluoromethyl)pyridine)dibromidocopper(II) (3)

A solution of copper(II) bromide (0.114 g, 0.500 mmol) in 15 mL of methanol was added slowly with stirring to a solution of 5-TFMAP (0.162 g, 1.00 mmol) in 6 mL of methanol resulting in a dark brown solution which was left covered with parafilm for slow evaporation at room temperature. After several days a teal precipitate of copper(II) hydroxide formed which was removed via gravity filtration. This was repeated once a week over the evaporation of the solution. Dark brown crystals formed at the bottom of the beaker after 3 weeks, which were recovered by vacuum filtration, washed with 2-methylpropan-2-ol and allowed to air dry to yield 0.063 g (26.63% yield). IR (KBr, ν in cm⁻¹): ν 3512 (m), 3406 m, 3320 m, 1638 s, 1567 m, 1519 m, 1419 m, 1322 s, 1277 w, 1168 m, 1154 m, 1115 s, 1080 m, 950 w, 927 w, 832 m, 629 (w) cm⁻¹. CHN Calc. for C₁₈H₁₅N₆F₉CuBr₂: C, 30.46; H, 2.13; N, 11.84. Found: C, 30.5; H, 2.11; N, 11.60%.

2.4. Synthesis of bis(2-amino-5-(trifluoromethyl)pyridine)dibromidocopper(II):2-amino-5-(trifluoromethyl)pyridinium bromide co-crystal (4)

A solution of copper(II) bromide (0.425 g, 1.81 mmol) in 15 mL of 50:50 water/propan-1-ol was added slowly with stirring to a solution of 5-TFMAP (0.594 g, 3.60 mmol) in 15 mL of 50% water/propan-1-ol resulting in a turbid sea-green solution which was left for slow evaporation at room temperature. A pale blue precipitate of copper(II) hydroxide (*vide supra*) was removed by gravity filtration three times over the course of a week. Dark blue crystals formed at the bottom of the beaker after eight days which were recovered by vacuum filtration, washed with 2-methylpropan-2-ol and allowed to air dry to yield 0.0023 g (0.24% yield). If stored at room temperature, the crystals would degrade within a week forming a white layer on the surface. The white layer could be removed by dissolution in toluene and recovered by evaporation of the solvent. It was shown by IR to be recovered 5-TFMAP. This decomposition process was significantly slowed when stored in the cold room, or if the crystals were stored in the mother liquor. IR (KBr, ν in cm⁻¹): 3460 (m), 3370 (m), 1650 (m), 1627 (m), 1572 (w), 1424 (w), 1328 (s), 1284 (w), 1120 (m), 1081 (m), 831 (w), 626 (w) cm⁻¹. Proper combustion analysis was not obtained (in spite of multiple attempts) due to the instability of the material.

2.5. X-ray structure analysis

Data for **1–4** were collected on an Agilent Technologies diffractometer using the CrysAlisPro software with Cu K α radiation ($\lambda = 1.54184$ Å) with ω -scans at 120.01(10) K employing a mirror monochromator. Cell parameters were refined using CrysAlisPro [18] and absorption corrections using spherical harmonics were

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