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Synthesis, structure, and magnetic properties of a family of copper(II) complexes and salts of isoquinoline: (isoquinoline)<sub>n</sub>Cu(X)<sub>2</sub> [X=Cl, Br] and (isoquinolinium)<sub>2</sub>CuX<sub>4</sub>(H<sub>2</sub>O)<sub>n</sub> [X= Cl, Br; n= 0,1]

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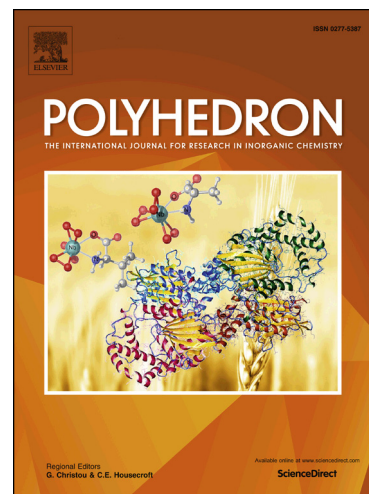
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**Synthesis, structure, and magnetic properties of a family of copper(II) complexes and salts of isoquinoline: (isoquinoline)<sub>n</sub>Cu(X)<sub>2</sub> [X=Cl, Br] and (isoquinolinium)<sub>2</sub>CuX<sub>4</sub>(H<sub>2</sub>O)<sub>n</sub> [X= Cl, Br; n= 0,1]**

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**Abstract:** The compounds (iQuin)<sub>2</sub>CuX<sub>2</sub> (X = Br (**1**), Cl (**2**)), (iQuinH)<sub>2</sub>CuBr<sub>4</sub>·H<sub>2</sub>O (**3**) and two polymorphs of (iQuinH)<sub>2</sub>CuCl<sub>4</sub> (**4**, **5**) (iQuin = isoquinoline) have been prepared and studied via X-ray crystallography and variable temperature magnetic susceptibility measurements. Compound **1** crystallizes in the monoclinic space group P2<sub>1</sub>/n while **3**, **4** and **5** all crystallize in the triclinic space group P-1. Magnetic susceptibility measurements for **1** are best fit by an antiferromagnetic alternating chain model ( $J/k_B = -56.6(2)$  K,  $J'/k_B = 5.1(8)$  K) although the crystal structure suggests a uniform chain. Compound **2** is well described as an isolated uniform antiferromagnetic chain ( $J/k_B = -25.6(1)$  K), while **3** agrees well with the antiferromagnetic rectangular model ( $J/k_B = -5.03(2)$  K,  $J'/k_B = -1.0(1)$  K). The two polymorphs, **4** and **5**, exhibit distinctly different behavior as **4** is well described by the 2D-square antiferromagnetic layer model ( $J/k_B = -4.24(2)$  K), but **5** crystallizes as well isolated magnetic dimers ( $J/k_B = -15.8(1)$  K). Magnetic superexchange is proposed to occur via either the bihalide or two-halide pathways. Finally, compound **6**, isoquinolinium tribromide) was isolated as a biproduct of the synthesis of **3** and was characterized via X-ray diffraction. The formation of the tribromide ion in situ provides support for the mechanism of electrophilic aromatic bromination reactions which have been previously observed in syntheses similar to that of **3**.

## Introduction

The field of molecular magnetism has erupted since the discovery of two-dimensional high-temperature, superconducting copper-oxide compounds.<sup>1</sup> Since then, the coordination chemistry and magnetism communities have been developing metal coordination compounds to better understand these superconducting systems.<sup>2,3</sup> In particular, several compounds of the general formula L<sub>n</sub>MX<sub>n</sub> and (LH)<sub>n</sub>[MX]<sub>n</sub> have been of interest as they may provide the same lattice type as is observed in the high T<sub>c</sub> superconductors, but with weaker magnetic exchange which allows for detailed study at accessible temperatures and magnetic fields.<sup>4,5,6,7,8</sup> These systems are particularly important for understanding magnetostructural correlations. Copper(II) is an attractive metal for study because of its d<sup>9</sup> electron configuration and spin of ½, making it a quantum system. With typical g-values near 2.1, copper's magnetic properties can frequently be treated as Heisenberg-like.<sup>9</sup> While the halide ions are typically responsible for the magnetic exchange observed between copper ions in these systems,<sup>10</sup> the ancillary species affect how the complexes pack into a three-dimensional lattice and they influence the geometry of the copper coordination sphere through their packing. Both of these factors impact the potential magnetic superexchange pathways and the resulting sign and strength of the magnetic exchange. The geometry of a four coordinate Cu(II) species ranges from tetrahedral<sup>11</sup> to square planar,<sup>12</sup> with a distorted tetrahedral geometry being the most common. The ancillary ligands may also isolate the copper(II) ion-containing species creating low-dimensional magnetic lattices.<sup>13</sup> The synthesis

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