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FULL PAPER

Regulating Noncovalent Interactions in Amino Amide Copper Complexes

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Abstract: The relevance of intermolecular noncovalent Cl•••Cu interactions in the magnetic and biological behavior of copper complexes derived from amino amides was studied. Crystallography studies showed that these complexes tended to stack favoring noncovalent interactions (hydrogen bonding and Cu•••Cl). However, the presence of substituents at the C10 and C13 positions regulated the supramolecular structures in **2**. Thus, magnetic studies at 93, 293 and 353 K demonstrated that magnetic exchange was favored only by Cu-Cl•••Cu interactions. Moreover, biological studies showed that only those copper complexes with ferromagnetic behavior present cytotoxic activity. Natural Bond Orbital (NBO) and Quantum theory of atoms in molecules (QTAIM) computations were used to corroborate the presence of the noncovalent interactions.

Introduction

Coordination chemistry has demonstrated use in the design of new substances and novel materials with novel physical and biological properties and unique functionalities.[1] For example, the structural behavior of coordination compounds can facilitate or restrict electronic exchange between metal centers and unpaired electrons.[2] This behavior has been adequately described by the Bleaney-Bowers expression for Cu^{II} complexes, which implicates the coupling of two metal centers by electronic exchange (EE) interactions.[3] Thus, EE could produce states with singlet (S = O) or triplet (S = 1) spin. Then, if the triplet state has lower energy, the system will have ferromagnetic behavior.

In later years, interest has increased on the study of magnetic exchange through noncovalent interactions (π-π stacking, hydrogen bonding, halogen bonding, etc.) because materials with weak magnetic behavior could be used in the design of new technologically advanced devices.[4] Some cases have been reported where noncovalent interactions favorably compete with covalent and coordination bonds in the propagation of magnetic exchange.[5] Thus, the modulation of noncovalent interactions has become a very important topic for the design of supramolecular systems with specific magnetic properties.

On the other hand, noncovalent interactions have an outstanding role in the biological activity of metal complexes.[6] For instance, DNA has binding number modes for interaction with coordination complexes. However, compounds with planar geometry and aromatic groups are useful as metallo-intercalators.[7] Thus, the presence of the metal center and aromatic groups favor the π-stacking of the coordination complex with the nitrogenous bases. Hence, the synthesis of molecules where noncovalent interactions favor stacking is relevant for the design of new compounds with significant biological properties.

We chose to study complexes **2** because amino amides **1** are tridentate ligands capable of forming planar coordination complexes with Cu^{II} as was reported by García-Orozco *et al* for compound **2a** (Scheme 1).[8] The presence of benzimidazolyl, amide, and amine groups will maximize the presence of π•••π and hydrogen bond interactions in these molecules. Thus, compounds **2** could easily stack upon crystallization and promote Cu-Cl•••Cu interactions. Additionally, the presence of R substituents on C10 and C13 might modulate the molecular stacking and regulate superexchange interactions. In this context, we used magnetometry and X-ray diffraction as tools to study the structural and magnetic behaviors of copper complexes **2**. Moreover, we resorted to Natural Bond Orbital (NBO) and Quantum Theory of Atoms in Molecules (QTAIM) studies of crystals **2a** and **2f** to

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