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Crystal Engineering: Stacking Interactions Control the Crystal Structures of Benzothiadiazole (btd) and Its Complexes with Copper(II) and Copper(I) Chlorides

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Crystal engineering and design of solid-state architectures has become an area of increasing interest in recent years.[1−3] One of the most significant goals in the field is to carry over robust modules or motifs from the crystal of one compound to that of another.[3] In the context of inorganic/organic hybrid materials, two different design philosophies have, so far, been employed: adjacent transition-metal complexes (discrete building blocks) are linked through either (i) coordinate covalent bonds[4−6] or (ii) hydrogen bonds.[7] Both approaches or their combinations[8,9] have resulted in the construction of few predesigned 2D or 3D supramolecular architectures.

Interactions between aromatic molecules represent an important class of intermolecular forces in chemistry, biology, and materials science.[10−12] They control a variety of molecular recognition and self-assembly phenomena, including the packing of aromatic molecules (and therefore the materials properties of these compounds) and template-directed synthesis. Hence, their significance in crystal engineering should not be underestimated.

An example of the role of stacking interactions is provided by the structure of the potentially bidentate bridging ligand 2,1,3-benzothiadiazole (btd), which consists[13] of columns of stacked molecules (intermolecular distance 3.50 Å) running along one of the crystallographic axes; there is no significant interaction between adjacent columns. The btd molecule has a fixed bridging angle, and its coordination chemistry has been rather neglected.[14,15] If the free ligand is reacted with suitable metal-containing starting materials, such as copper(II) and copper(I) chlorides, an additional structure-determining factor is introduced, namely the coordination bond. We wish to show here how the aromatic stacking interactions are able to create a structural frame strong enough to determine the dimensionality and the nature of the resulting network independently of the two different metal oxidation states.

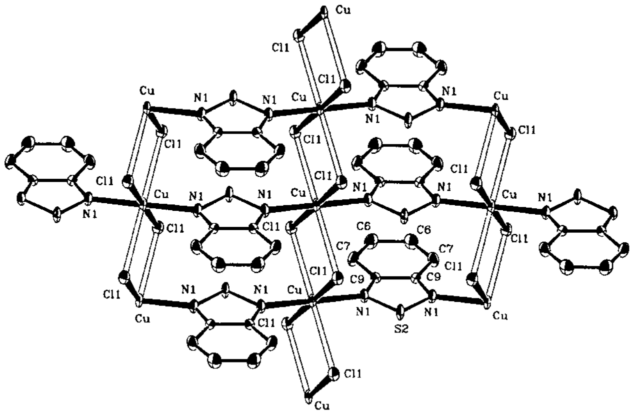

Figure 1. Structure of **1** showing a single 2-D layer (*ab* plane). The open lines indicate the weak Cu−Cl bonds.

Reaction of btd with $CuCl_2{\cdot}2H_2O$ in a 1:1 molar ratio in Me_2CO gives a yellow-green solution from which $[CuCl_2(btd)]_n$ (**1**) precipitates within 1−2 min. Layering of an MeCN solution of the microcrystalline powder with an equal volume of Et_2O/*n*-hexane (2:1) gives yellow crystals of **1** in ca. 70% total yield. The solid consists[16] of 1-D $\{Cu(\mu\text{-}Cl)_2\}_n$ linear chains running along the *a* axis linked via μ-btd ligands along the *b* axis to afford an extended 2-D layered network (Figure 1). The intranetwork Cu···Cu separations are 3.719(3) Å (via chlorides) and 6.307(6) Å (via btd), while the shortest internetwork Cu···Cu separation is 8.800(6) Å. The Cu^{II} atom sits on an inversion center, while a mirror plane, perpendicular to the btd plane, passes through S. Each Cu^{II} atom is octahedrally coordinated to four Cl^- ligands and two btd molecules. The Jahn−Teller distortions are clearly evident in the Cu−Cl distances (2.272(1) and 2.831(1) Å). The Cu−N bond length is 2.088(3) Å. Complex **1** has a similar structure with $[CuCl_2(pyz)]_n$ (pyz = pyrazine).[17]

The reaction of btd with 1 equiv of CuCl in $MeNO_2$/MeCN in air gives a yellow solution which, after ca. 70% volume reduction in vacuo, slowly produced a microcrystalline red powder of $[CuCl(btd)]_n$ (**2**) in 10−15% yield; addition of a double volume of Et_2O increases the yield to ca. 60%. Red crystals of **2** suitable for X-ray diffraction studies were grown by slow evaporation of an MeCN/Me_2CO (1:1) solution of the microcrystalline solid. Complex **2** can also be prepared in good yield (60%) and high purity by reduction of a solution of **1** in MeOH under reflux by a clean wire of Cu and subsequent addition of a further quantity of btd (1 equiv). The structural characterization[18] of this complex reveals the formation of 2-D sheets in which a split-stair $\{CuCl\}_n$ motif is observed (Figure 2). Within each layer the metal ions are bridged by two Cl^- ligands and two btd molecules. Atoms Cu and Cl sit on 2-fold crystallographic axes while a mirror plane, perpendicular to the btd plane, passes through S. The layers consist of two types of perpendicular zigzag chains crossing at the Cu^I atom. The $\{Cu(\mu\text{-}Cl)\}_n$ chains run along the *a* axis (Cu···Cu = 3.840(2) Å) and the $\{Cu(\mu\text{-}btd)\}_n$ ones along the *b* axis (Cu···Cu = 6.114(5) Å); the shortest internetwork Cu···Cu separation is 8.093(5) Å. Within the coordination polyhedron the Cu−Cl and Cu−N bond lengths are 2.372(10) and 2.017(3) Å, respectively. Complex **2** joins a

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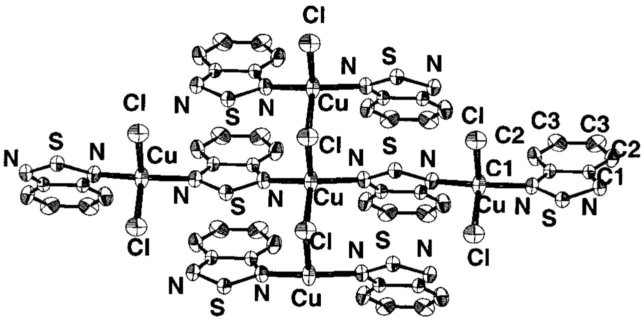

Figure 2. Structure of **2** showing a single 2-D layer (*ab* plane).

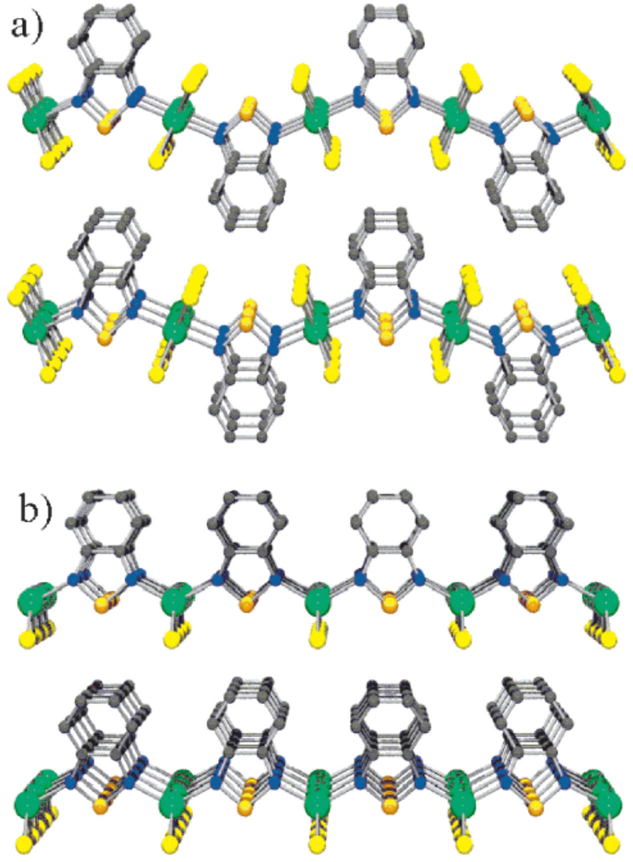

Figure 3. Packing diagrams of **1** (a) and **2** (b), viewed approximately down *a*. Two layers are shown in each case.

small family of $[\mathrm{CuX(L{-}L)}]_n$ complexes (X = Cl, Br, I; L−L = bidentate bridging N-donors) with a somewhat similar layered structure.[19−21]

A characteristic structural feature common to free btd, **1**, and **2** is the existence of strong face-to-face *intra*layer stacking interactions between the btd ligands along the *a* axis (Figure 3). The btd molecules form columns within the crystal lattice, with the interplanar distances being 3.50, 3.63, and 3.46 Å for free btd, **1**, and **2**, respectively. Within the stacks each btd is shifted, with respect to the one below it, along the long axis of the molecule, so that each S atom sits approximately over the middle of the five-membered ring below it (Figure 4). This is the reason that the interplanar distances are controlled not by the large size of the S atom but by the classical ring to ring interactions. In **1** the columns are oriented on alternating sides of each sheet, while in **2** the btd ligands all lie on the same side of the layer. In addition to the van der Waals interactions, there are also short C···Cl distances in **1** (C7···Cl1($-x$, $-y$, $1-z$) = 3.444(4) Å and C7−H7···Cl1($-x$, $-y$, $1-z$) = 123(2)°, C7···Cl1($1-x$, $-y$, $1-z$) = 3.519(4) Å and C7−H7···Cl1($1-x$, $-y$, $1-z$) = 126(2)°) and **2** (C3···Cl(x, y, $1+z$) = 3.644(5) Å and C3−H3···Cl(x, y, $1+z$) = 156(4)°), possibly indicating weak C−H···Cl hydrogen bonds.[20,22] Recently, several groups have demonstrated[23−25] the dramatic enhancement of the acceptor capability of chlorine imparted by coordination to metal centers, relative to organochlorine. For example, such weak C−H···Cl−M interactions have been observed in the crystal structures of the 2-D polymers $[\mathrm{CuCl(pyz)}]_n$[20] and $[\mathrm{CdCl_2(pyz)}]_n$.[24]

The magnetochemical study of the 2-D coordination polymers is of great current interest because these compounds are candidates for molecule-based magnets.[26] Molecule-based magnets are molecular compounds exhibiting a spontaneous magnetization below a critical temperature (T_c). They are anticipated to exhibit a plethora of technologically important attributes that include modulation/tuning of properties via coordination chemistry methodologies, compatibility with polymers for composites, low density, transparency, flexibility, low-temperature processibility, electrical insulation, solubility, high coercivity, high strength, low enviromental contamination, biocompatibility, high magnetizations, semiconducting behavior, etc.[26] Many of the nonmagnetic characteristics are not available with conventional atom-based magnets (metals, oxides, alloys).

Solid-state magnetic susceptibility measurements were performed on **1** in the range 3.0−300 K, in a 1 kG applied magnetic field (Figure 5). There is a maximum in χ_M at ca. 35 K; below 11 K a Curie tail is seen. The high-temperature value of $\chi_M T$ per copper(II), not fully saturated, is 0.37 emu mol^{-1} K, almost identical with what would be expected for isolated $S = {}^1/_2$ Cu^{II} atoms. The exchange interaction through the pathway provided by the axial bonding (via the chloro bridges) is expected to be negligible due to the low unpaired electron density along the d_{z^2} orbital in the axially elongated octahedral coordination around the Cu^{II} atoms. The main pathway for exchange interactions is the long one, and it proceeds through the equatorially coordinated btd ligands; thus, a linear-chain model was tried. The data were fitted by the equation[27]

$$\chi_M = \frac{N\mu_B^2 g^2}{kT}\,\frac{0.25 + 0.14995y + 0.30094y^2}{1.0 + 1.9862y + 0.68854y^2 + 6.0626y^3}\,(1-\rho) + NS(S+1)\frac{g^2\mu_B^2}{3kT}\rho$$

where $y = J/kT$, ρ is the fraction of mononuclear impurities (real and/or finite-chain effects), and the other symbols have their usual meaning. A very good fit was obtained with $J = -20.1$ cm^{-1}, $g = 2.1$, and $\rho = 2.3\%$. This J value is similar to the values reported for other polymeric copper(II) complexes containing a single, equatorially coordinated azole ligand as the main exchange pathway.[28] The exchange interactions through the chloro ligands (if any), expected to show up at low temperatures, are blurred by the presence of ρ and cannot be correctly assessed.

In summary, upon complex formation with $\mathrm{CuCl_2}$ or CuCl the orientation of the btd columns does not remain the same as in the crystal structure of the free ligand, as expected; however, the columns are maintained in the crystal structures of the two complexes (Figure 4). Thus, the columns of stacked btd molecules are carried over from the crystal structure of the free ligand to the crystal

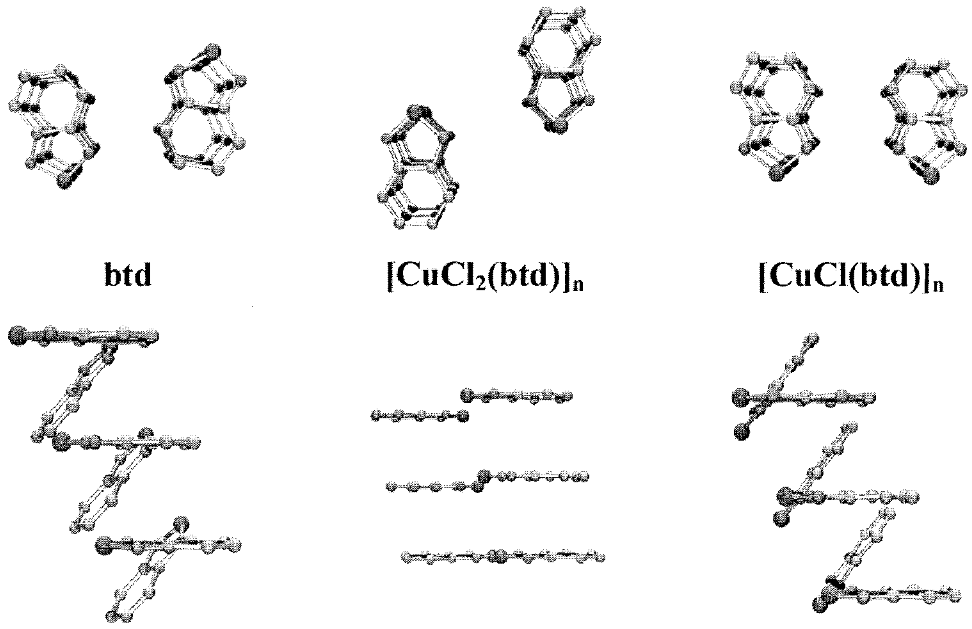

Figure 4. Two adjacent stacked btd columns in the crystal structures of the free ligand (left), complex **1** (middle), and complex **2** (right): (top) face view; (bottom) side view.

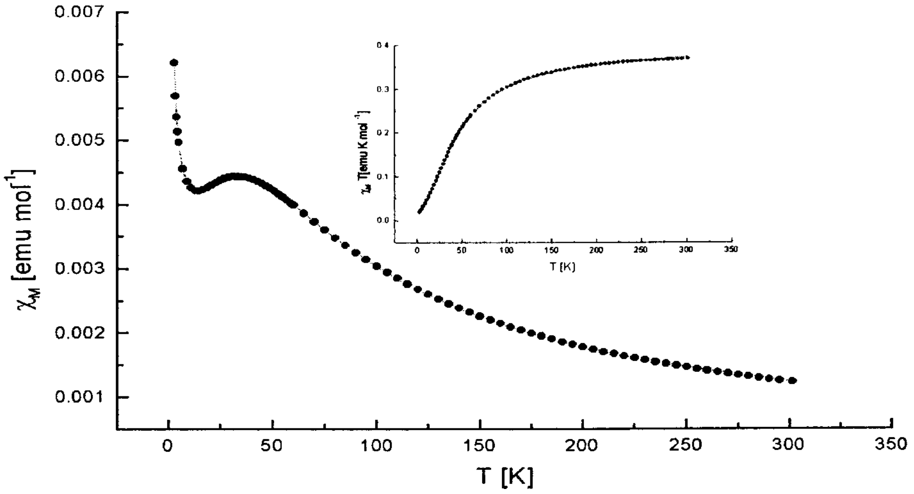

Figure 5. Plots of χ_M vs T and $\chi_M T$ vs T (inset) for a polycrystalline sample of complex **1**. The solid line represents the fit to the theoretical model; see the text for the fitting parameters.

structures of the two complexes (which contain two ions of the same metal with different coordination chemistry), serving as "macroscopic" templates on which the copper–halogen chains are assembled/fitted in such a way that the resulting structures preserve the information of the intermolecular interaction. This conclusion is strengthened by our recent results on other MX_2/btd systems (M = Mn, Fe, Co, Ni; X = Cl, Br, I), giving the message that understanding and utilization of $\pi-\pi$ stacking is of great importance for the further development of (inorganic) supramolecular chemistry and the tuning and prediction of crystal structures.[12] However, the strand-like nature of the Cu–Cl substructures, which can nicely fit between the stacks, may also help the formation of the observed structures, as suggested by the fact that other metal–inorganic ligand (*e.g.* NO_3^-) combinations affect[14] the btd–btd stacking interactions. Most probably the predisposition of the btd molecules to form extended $\pi\cdots\pi$ arrays and the ability of Cu–Cl to form extended polymeric species are complementary and act in concert to give these structures.

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Supporting Information Available: X-ray crystallographic information files (CIF) are available for compounds **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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