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Supramolecular assembly in metal complexes: Two structural cases*

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Abstract: With the current advances in our understanding of molecular components in the solid-state world, the relation between energy and geometry remains controversial. In this study, we deliver a concise account for supramolecular chemistry, and in order to illustrate some of its concepts we describe some structural and theoretical analyses for two unique cases of our work. We elaborate on a supramolecular model of controlled "one-pot" host–guest metal-mediated self-assembly reaction inside iron coordination polymer grid architecture, and we review halogen bonding by specifically observing M–Cl•••Cl–M intermolecular interactions using Cambridge Structural Database (CSD) hit analyses with theoretical calculations.

Keywords: coordination complexes; halogen bonding; self-assembly; supramolecular chemistry; X-ray single-crystal diffraction.

INTRODUCTION

One can describe supramolecular chemistry as a fairly new field that has emerged in-between biochemistry, chemistry, and materials science. Owing to the broad interest that comes from its intersection with science and technology, also with the absence of clear domain borderlines, the field of supramolecular chemistry is blossoming [1–3]. Supramolecular chemistry is developing its own language, so we currently define the *supramolecule*, the motor of supramolecular chemistry, as basically a set of molecular components held together by intermolecular interactions. These diverse, relatively weak but directional interactions are able to change the properties and functions of the whole association.

It is widely accepted that supramolecular chemistry has appeared to show two distinctive areas that differ by the examined subject and the implemented tool. The first one deals with molecular assembly of inclusion compounds. The host–guest chemistry and the key–lock mechanism are the fundamental subjects of this domain, and templated organic synthesis is the tool. Specifically, the hosts are mainly organic macrocyclic molecules, and neutral molecules or metal salts serve as guests. From this domain is the chemistry of miscellaneous molecular architectures like cyclodextrin, crown ether, cryptands, catenanes, and rotaxanes [4], while traditional coordination complexes formed by transition-metal ions with nitrogen-based macrocycles like porphyrins, corrins, or chlorins represent the marginal cases. Concepts like molecular recognition and self-organization were introduced and rationally developed to justify the interlocking mechanism [5]. The second flourishing area is termed "crystal engineering", which is the priori design of solid crystals with desired properties. These compounds are typically coordination complexes of multidentate organic ligands with synthetic-controlled design over structure. Crystal engineering is intimately linked to inclusion chemistry with concepts like self- and

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supramolecular assembly. Thus, crystal engineering can be considered as supramolecular chemistry at the solid-state phase [6,7].

In the current study, we elaborate on these two fields with two case studies from our research. The first case deals with the host–guest interactions in the self-assembly reaction of Fe^{II} inclusion coordination polymer. Secondly, we analyze the lately observed halogens M–Cl···Cl–M intermolecular interactions, by using Cambridge Structural Database (CSD) hit analysis. Although these two cases are mutually independent and distantly related, they are represented here for indicating the intersection between inclusion chemistry and crystal engineering in the scope of supramolecular chemistry.

SUPRAMOLECULAR ASSEMBLY AND CRYSTAL ENGINEERING

Crystal engineering is shown as a separate area in-between inorganic, solid-state chemistry and materials science within the framework of supramolecular chemistry. Reports [8–11] on the population analyses of the geometrical and noncovalent interactions in organic and metal–organic structures, with experimental advances in single-crystal X-ray and neutron diffractions, have paved a way for the current understanding of these forces. The scope of modern crystal engineering is expanding, so that besides synthesis and analysis there is also structural prediction, Monte Carlo simulation, and density functional theory (DFT) studies [12].

Crystal engineering employs molecular building blocks that are assembled via covalent or noncovalent synthesis to produce functional solid materials. The covalent/coordination synthesis uses strategies based on a priori hypothesis for a number of convergent binding sites in the organic ligand and the preferred coordination geometry of the metal centers. The reasonably predictable result is an extended framework structure of high stability constructed from the simpler molecular building block self-assembly. On the other hand, noncovalent synthesis uses the intermolecular forces to construct supramolecular architectures [13]. It differs from covalent/coordination synthesis, as being less stable and difficult to predict. Owing to the level of complexity encountered during the prediction of structures based on noncovalent synthesis, precise tactics for intermolecular synthesis are still in a stage of development [7]. Nevertheless, both types of synthesis are carried out via the same step, noted as molecular self-assembly.

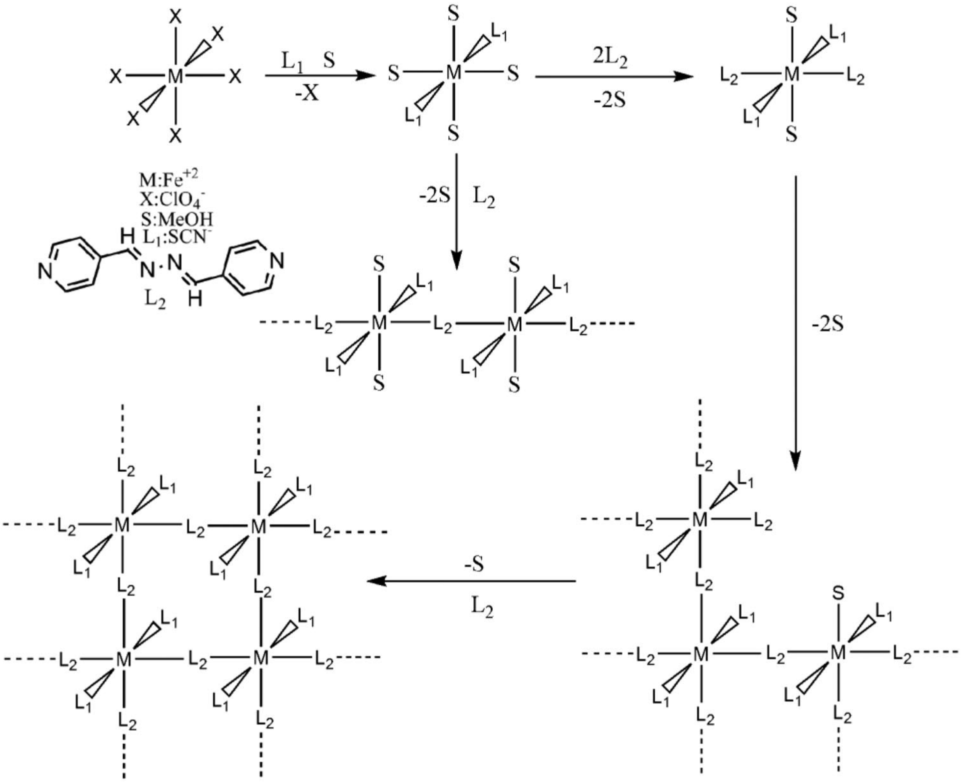
Molecular self-assembly is the tool of crystal engineering that is the designing of molecular blocks and interactions so that chemical selectivity and shape complementarities will yield an aggregation of the desired structure. The concept of *supramolecular synthon* was an important leap in crystal engineering. The term "synthon" describes molecular building units that, during the noncovalent synthesis, participate in specific structural pathways, thus producing a predictable structural interaction [14]. Intermolecular interactions can be basically classified into isotropic van der Waals (e.g., π–π stacking) and anisotropic Coulombic forces (e.g., hydrogen bonds, halogen···halogen interactions). What give each of these interactions its unique character are the distance dependence, energy, and directionality. Hydrogen bond supramolecular synthons are perhaps the most common and obvious code; it is the supramolecular master key interaction [3]. Hydrogen bonding was observed a century ago [15] and was initially defined by Pauling [16]. Although it is generally weaker than the covalent bond, the strong hydrogen bond is more energetic than the weak covalent bond [10,11]. Also, there are cases where both chemical and geometrical aspects of intermolecular interaction are interlinked, thereby allowing for certain interactions such as halogen···halogen (e.g., Cl, Br) or chalcogen···chalcogen (e.g., S, Se) interactions to be regarded as supramolecular synthons [17].

In the following discussion, we will use two models from our research to illustrate both kinds of covalent and noncovalent self-assembly and to demonstrate how both strong and weak interactions are contributing to the whole molecular assembly.

SELF-ASSEMBLY INSIDE COORDINATION GRID INCLUSION COMPLEX

The design, synthesis, and study of coordination polymers supramolecular hosts constitute a central theme in metal–organic supramolecular chemistry [1,6]. The interest is unlimited to their inherently beautiful high-symmetry assemblies or possibility of synthetic control, but also to their higher rigidity, thermal stability, and low solubility. In the covalent/coordination synthesis, the metal coordination bond is a strong directional interaction capable of inducing an abundance of various supramolecular architectures. Extensive topological collection of chains, ladders, grids, honeycombs, cages, or helicates were all formed and reported [6,7], depending on the nature of the metal and ligands, which both are holding the codes for the assembly process [2].

In principle, square (4,4) grids are assembled as 2D channels of coordination polymers with variable void sizes. In this perspective, monodentate *N*-ligands were employed intensively [18]. Compared to *O*-donor ligands, the bridging 4,4'-bipy derived ligands are limited in their influence on the network structure since the ligand is able to occupy a single metal coordination site at orthogonal position, thus bridging metal centers in a manner that is controllable to some extent [1]. A study on this process allowed us earlier [19] to design a supramolecular self-assembly reaction, based on Fe^{II} metal centers. The 4,4'-bipyridine derivative, 1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene, and Fe^{II} metal centers were used to construct either 1D linear chain coordination polymer [20] or 2D square grid supramolecular host framework [21], Scheme 1. Intentionally, the latter was used as an inclusion host for cationic, anionic, and neutral guests during the self-assembly, while rules of crystal engineering were used to modify the type of guests interlocking inside this host. Such a reaction is individually represents the two supramolecular perspectives of inclusion compounds and crystal engineering.



Scheme 1 Proposed self-assembly reaction mechanism for the molecular 1D chain and 2D square coordination grid.

Considering the $Fe(ClO_4)_2{\cdot}xH_2O$ reaction at room temperature with KSCN gives rise to the $Fe^{II}(SCN)_2$ and a precipitate of $KClO_4$. The higher stability of $KClO_4$ compared to $Fe(ClO_4)_2$ drives the reaction to completion. The reaction under N_2 is essential to protect Fe^{II} from oxidation to Fe^{III}. Careful stoichiometric drop-wise addition of 1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene monodentate ligand in EtOH turns the solution a purple color and results in the condensed phase compounds of either the 2D square grid or the 1D chain topology. The open ligation sites of metal centers are temporarily filled by weakly coordinated solvent molecules, then the self-assembly process continues until formation of the most stable product is complete. Also favoring the product is the enthalpy released upon replacement of weak metal–solvent bonds with somehow stronger metal–ligand bonds; therefore, the choice of solvent is important.

The 2D coordination supramolecular grids, based on Fe^{II} octahedral metal centers, are formed with a dimension of 1.57 × 1.57 nm. In fact, most molecular squares crystallize as 1D nano-scale molecular sieve of channels containing materials [1,22]. The initial aim of this work was to create the host grids without guests. However, the crystalline solid products are obtained only in the presence of guest molecules that were either Fe^{II} or Ru^{II} tris(1,10-phenanthroline), both X-ray single-crystal structure projections are depicted in Fig. 1, left and middle, respectively. The high rigidity and preorganization capacity enable the perfect square grids to accommodate $Fe^{II}(phen)_3$ metal cations, water molecules, as well as the neutral 1,4-bis(4-pyridyl)-2,3-diaza-1,3 butadiene ligand molecules with additional crystallographically disordered perchlorate ions. Thus, ca. 20 % of the unit cell volume is a "virtual" accessible solvent voids, as calculated [23]. According to the classification of porous coordination polymers developed by Kitagawa [22], the current case represents the first generation of porosity in coordination polymers.

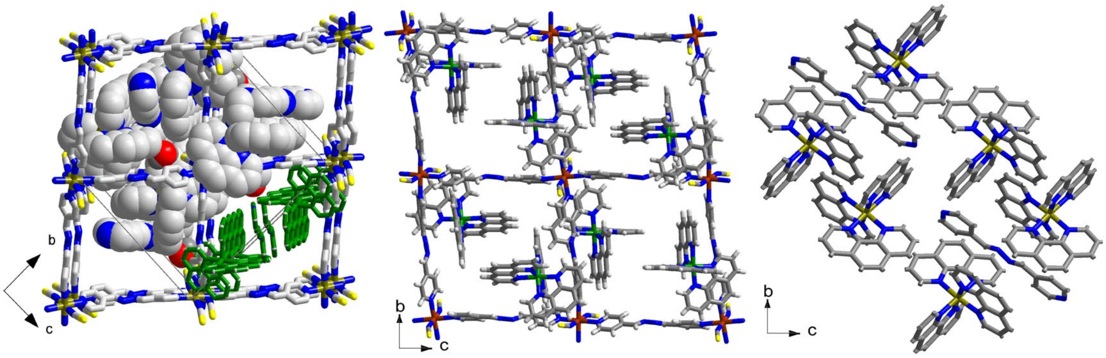


Fig. 1 Projections in crystal structures of 2D Fe^{II} coordination polymer with Fe^{II}tris1,10-phen (left), with Ru^{II}tris1,10-phen (middle), and independent guest assembly (right).

Certainly, the reaction is an in situ self-assembly where guests like neutral molecules and metal cations exist at the same time as the host grids are constructed, thus self-assembly uses the best conformation that minimizes the thermodynamic barriers. One of these conformational modifications is the –C=N–N=C– torsion angle decrease from 180º in the case of neutral ligand [24] to 162.86º in the case of the square grid. Although some reports described cases of 2D host coordination polymers bearing guests [6,7], the current case uniquely features solvent molecules with neutral, cations and anions; organic and inorganic types of guests are self-assembled via one reaction. Moreover, we were able to "engineer" the types of guest cationic parts, so that from the $Fe^{II}(phen)_3$ to the Ru^{II} analogue, an isostructural inclusion compound is formed and a minor change in unit cell dimensions vs. unit cell voids is observed. It is also noted that this host lacks any racemic resolution capacity, so that both Λ and Δ $M^{II}(phen)_3$ exist in the solution and eventually in the crystals. The metal cations guests $M^{II}(phen)_3$

bind with the host square grids via many π–π interactions at distances in range of 3.5–3.7 Å and with 1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene free ligands via other π–π and σ–π interactions at H···π average distance of 2.86 Å. In order to elucidate the possible interaction modes in-between the guests without the host, guest molecules were reacted independently and the neutral bis(4-pyridyl)-2,3-diaza-1,3-butadiene free ligand was crystallized with $Fe^{II}(phen)_3$ complex [21], Fig. 1 right. The $Fe^{II}(phen)_3$ interacts with 1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene by virtue of many C–H···π at average H···π distance of 2.81 Å as well as π–π interactions at average centroid···centroid distance of 3.62 Å. The convergent sites inside the host grid at –C=N–N=C– organic linker are mainly the reason for the interactions between the host and guests. These similarities in π–π and C–H···π interaction modes between guest molecules, with and without the host, were also theoretically justified by near Hartree–Fock quantum calculations and graphically presented by Hirshfeld surfaces mapping. The readers are referred to more structural and technical descriptions as given in [21].

In fact, the supramolecular *motifs* existing in-between inclusion molecules inside the (4,4) grid are comparatively the same when these guest molecules are allowed to crystallize independently, and this in turns reveals the weak effect of the 2D grid formation (covalent/coordination synthesis) on the intermolecular interactions (noncovalent synthesis) in-between the guests. To sum here, we represent a case where molecules in a pure system assemble to exhibit supramolecular motifs, quite similar to those it will adopt if allowed to crystallize with a host compound.

M–Cl···Cl–M HALOGEN INTERMOLECULAR INTERACTIONS

Beside conventional and nonconventional hydrogen bonds, there is a growing interest in other atom–atom interactions that act as crystal engineering synthons [14]. The crystal short contacts (smaller than the sum of van der Waals radii $2r_{vdW}$), involving halogens or chalcogens atoms like Cl, Br, I, S, Se, etc., are always ascribed to induced dipole polarizable forces, hence directional with comparable strength to hydrogen bond. Halogens bond is a unique structural motif in crystal engineering [25]. A thermotropic smectic type A liquid crystal with transition temperature of 84 °C was self-assembled, during a reaction of halogenated benzene and alkoxystilbazole, via only halogen-bonding supramolecular interactions [26]. Since both initial components were non-mesomorphic, the halogen bonding is a special case for intermolecular noncovalent interaction inducing mesomorphism from non-liquid-crystalline reactants.

The term "halogen bond", an interaction involving halogens without hydrogen, is used to describe a broad range of interactions. Aside from D–H···X or D–H···X–M non-classical halogen-involved hydrogen bonding, the halogen bondings involve D···X–C, D···X–M (D: donor, i.e., C, N, or O, X: halogen, M: metal) with also atom–atom D–X···X–D, D–X···X–M, and M–X···X–M interactions. The inter-atomic halogen bonding, with halogen atoms acting as both nucleo- and electrophiles, was critically observed and defined [27–29], as a directive polarizability exists between the two halogen atoms in the crystalline solid due to nonspherical anisotropical charge distribution (known also as polar flattening [30,31]) at the halogen atoms. According to the model [32], the interaction population is classified into type I and type II interactions relying on the two C–X···X and X···X–C θ_1 and θ_2 angles. Type II interaction shows angles of ca. $\theta_1 = 90°$ and $\theta_1 = 180°$, thus representing the anisotropic polarization model, while type I with equal angles $\theta_1 = \theta_2$ around 110° is a consequence of geometrical restrictions, i.e., crystallographic symmetry [27–33]. During this dialogue between energy and geometry, halogen bonds were effectively explored in crystal engineering for the design of supramolecular aggregates [33–36].

Earlier, we [37] and others [38] demonstrated some aspects of organic carbon-bonded halogen C–X···X–C interactions, while the reports [39,40] on M–X···X–C hybrid inorganic–organic halogen systems verified a greater anisotropic potential associated with the more polar inorganic M–X bond. Recently [41], we identified Cu–Cl···Cl–Cu halogen supramolecular motifs in the oxido-*hexa*(μ-chlorido)*tetra*(2-(3-pyridyl)ethane-1-ol) *tetra* Cu^{II} coordination complex by DFT theoretical study, and here we are exploring inorganic bounded halogen interactions by means of CSD hit analysis. Figure 2 depicts scattergrams of M–Cl···Cl (θ_1) vs. Cl···Cl–M (θ_2) (left) and specifically Cu–Cl···Cl vs. Cl···Cl–Cu (right) angular distribution in CSD fragments search [42]. 1974 hits were encountered for M–Cl···Cl–M, from which 330 hits were found with Cu–Cl···Cl–Cu short contacts, out of a total of 19 420 hits with M–X···X–M interactions. In both M–Cl···Cl–M and Cu–Cl···Cl–Cu, we have roughly as many hits on the diagonal as off, those on the diagonal represent type I. The off-diagonals occur in the region θ_1: 120º–160º and θ_2: 40º–60º and are thus of "type II". The distribution is very similar to those of C–X···X–C and M–X···X–C ratios, but with less populations.

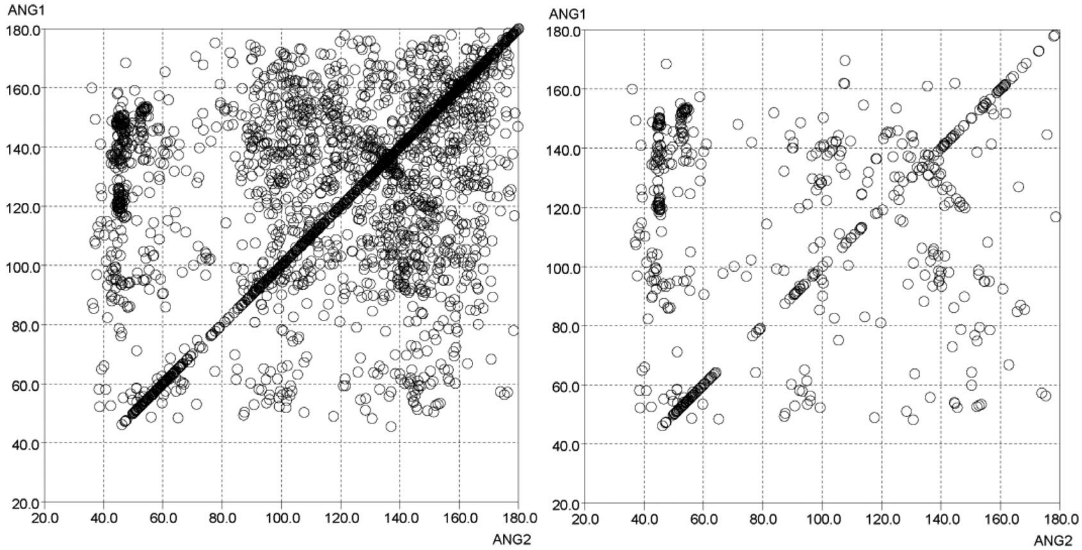


Fig. 2 Scattergrams for the M–Cl···Cl–M (left) and Cu–Cl···Cl–Cu (right) angular distribution for interaction distances between 3.0 and 3.7 Å.

In the solid-state phase of oxido-*hexa*(μ-chlorido)*tetra*(2-(3-pyridyl)ethane-1-ol) *tetra* Cu^{II} [41], the chlorido-bridged tetra-nuclear Cu^{II} clusters were assembled, via both O–H···O rings motif hydrogen bonds as well as Cu–Cl···Cl–Cu atom–atom interactions (Cl···Cl contacts of 3.498 Å; less than $2r_{vdW}$ with $\theta_1 = \theta_2 = 139.4°$; relevant to type I), into a 1D ribbon-like supramolecular assembly [41]. Due to the presence of both O–H···O and Cu–Cl···Cl–Cu and for the sake of structural motif identification, we carried out DFT calculations. The highest occupied molecular *p*-orbitals (HOMOs) on the two chloride atoms engaging in this interaction are populated with a large volume in the same direction of Cu–Cl bonding vectors, while a much smaller volume of HOMOs on the other two chloride atoms are uninvolved in this interaction and are perpendicularly aligned on Cu–Cl bonding vectors. Also, the lowest delocalization parameters are located at the hydroxyl oxygen atom as well as at the interaction-involved chloride atoms. With glide plane symmetry and *C*2/*c* crystallographic space group symmetry in the structure of oxido-*hexa*(μ-chlorido)*tetra*(2-(3-pyridyl)ethane-1-ol) *tetra* Cu^{II} and without theoretical evidences on anisotropic flattening, the overlap of MOs on the two chloride atoms is the cause of this intermolecular Cu–Cl···Cl–Cu atom–atom interaction. Also, the energy associated with the Cu–Cl···Cl–Cu and O–H···O interactions are of comparable strength, hence evincing the role of halogen atom···atom interactions in the presence of a more polarizable hydrogen bonding.

To conclude, the synergistic interplay of intermolecular noncovalent interactions must be considered as a single interrelated entity, and irrespective of the reason, the halogen short contacts appear to have a unique role in some cases of supramolecular structures.

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