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Editorial

Non-Covalent Interactions in Coordination and Organometallic Chemistry

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Abstract: The problem of non-covalent interactions in coordination and organometallic compounds is a hot topic in modern chemistry, material science, crystal engineering and related fields of knowledge. Researchers in various fields of chemistry and other disciplines (physics, crystallography, computer science, etc.) are welcome to submit their works on this topic for our Special Issue "Non-Covalent Interactions in Coordination and Organometallic Chemistry". The aim of this Special Issue is to highlight and overview modern trends and draw the attention of the scientific community to various types of non-covalent interactions in coordination and organometallic compounds. In this editorial, I would like to briefly highlight the main successes of our research group in the field of the fundamental study of non-covalent interactions in coordination and organometallic compounds over the past 5 years.

Keywords: non-covalent interactions; crystal engineering; organometallic compounds; coordination compounds; crystalline materials; supramolecular systems

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Non-covalent interactions in coordination and organometallic compounds (hydrogen, halogen, chalcogen, pnictogen, tetrel and semi-coordination bonds; agosic and anagosic interactions; stacking, anion-/cation-π interactions; metallophilic interactions, etc.) are topical in modern chemistry, material science, crystal engineering and related fields of knowledge. Both experimental and theoretical methods are widely used for the investigation of the nature and various properties of such weak contacts in gas, liquid and solid states. Non-covalent interactions could be the driving force in the design of smart materials with valuable redox, electronic, mechanical, magnetic and optical properties, and they are promising for the manufacture of LEDs, photovoltaic cells for solar power plants, porous structures, sensors, battery cells and liquid crystals.

In this editorial, I would like to briefly highlight the main successes of our research group in the field of the fundamental study of non-covalent interactions in coordination and organometallic compounds over the past 5 years.

Our group reported the first examples of the unambiguous identification of halogen bonding between metal centers and halocarbons [1] and the application of p-trifluoromethylbenzonitrile moiety for crystal engineering utilizing π-stacking: efficient π-stacking with benzene provides a 2D assembly of *trans*-($PtCl_2$ (*p*-$CF_3C_6H_4CN)_2$) [2]. We published several works about the recognition of the π-hole donor ability of iodofluorobenzenes [3,4]. In particular, we found that structure-directing weak interactions with 1,4-diiodotetrafluorobenzene convert 1D-arrays of ($M^{II}(acac)_2$) species into 3D-networks [5]. The metal-involving halogen bond Ar–I···($d_{z^2}Pt^{II}$) in a platinum acetylacetonate complex was discussed in [6]. We observed that the difference in energy between the two distinct types of chalcogen bonds drives the regioisomerization of binuclear (diaminocarbene)Pd^{II} complexes [7]. The intra-/intermolecular bifurcated chalcogen bonding in the crystal structure of thiazole/thiadiazole derived binuclear (diaminocarbene)Pd^{II} complexes was studied in [8]. The effect of $\mu_{(S,N-H)}$Cl contacts on the dimerization of Cl(Carbene)Pd^{II} species was discussed in [9]. The effect of π-hole···π non-covalent bonding on the conformational stabilization of acyclic diaminocarbene complexes and ligation-enhanced π-hole···π interactions involving isocyanides was analyzed in [10]. The (isocyano group π-hole)···($d_{z}{}^{2}$-M^{II}) interactions at (isocyanide)(M^{II}) complexes, where positively charged metal centers (d^8M = Pt, Pd) act as nucleophiles, were reported in [11]. The (isocyano group)···lone pair interactions involving coordinated isocyanides were discussed in [12]. In addition, we reported that intramolecular hydrogen bonding stabilizes *trans*-configuration in mixed carbene/isocyanide Pd^{II} complexes [13]. We fixed the solid state stabilization of unstable hemiketal ligands in copper(II) complexes due to the formation of a intermolecular hydrogen bond network [14] and the stabilization of redox reactive (RNC)Cu^{II} species in crystals via a halogen bond with I_2 [15]. We showed that intramolecular non-covalent B–H···π(Ph) interaction determines the stabilization of the configuration around the amidrazone C=N bond in *closo*-decaborato amidrazones [16]. We discovered the potential of diiodomethane as a halogen bond donor toward metal-bound halides [17]. Furthermore, other dihalomethanes were also considered as bent bifunctional building blocks for the construction of metal-involving halogen bonded hexagons [18]. In [19], we introduced a concept of four-center nodes: supramolecular synthons based on cyclic halogen bonding. A nice example of halogen contact-induced unusual coloring in the Bi(III) bromide complex due to anion-to-cation charge transfer via Br···Br interactions [20] and the electrophilic–nucleophilic dualism of nickel(II) toward Ni···I non-covalent interactions, viz. the semicoordination of iodine centers via the electron belt and halogen bonding via the σ-hole [21] were reported. The role of solvent···complex halogen bonding in the dramatically enhanced solubility of halide-containing organometallic species in diiodomethane was discussed in [22]. We describe several interesting examples of reverse arene sandwich structures based upon π-hole···(M^{II})(d^8M = Pt, Pd) interactions, where positively charged metal centers play the role of a nucleophile [23], and reverse sandwich structures from interplay between lone pair–π-hole atom-directed C···$d_{z}{}^{2}$(M) and halogen bond interactions [24]. The halogen bonding-assisted assembly of bromoantimonate(V) and polybromide-bromoantimonate-based frameworks was reported in [25]. The features of halogen bonding in the solid state structures of one- and two-dimensional iodine-rich iodobismuthate(III) complexes were discussed in [26]. The chlorotellurate(IV) supramolecular associates with "trapped" Br_2 via non-covalent halogen···halogen interactions were analyzed in [27]. The phenomenon of halogen bonding in isostructural Co(II) complexes with 2-halopyridines was fixed in [28]. The hexaiododiplatinate(II) as a useful supramolecular synthon for halogen bonds involving crystal engineering was considered in [29]. The supramolecular polymers derived from the Pt^{II} and Pd^{II} Schiff base complexes via C(sp^2)–H···Hal hydrogen bonding were reported in [30] and [31]. Finally, recently, the supramolecular self-organization via bifurcated $(N–H)_2$···Cl contacts that is responsible for the solid-state fluorescence of 1,2,4-triazole zinc(II) complexes was described in [32].

I hope that other authors will follow my initiative and that readers of this Special Issue of Crystals will have the opportunity to become acquainted with the achievements of researchers in this modern topic.

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