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THE ROLE OF HALOGEN BONDING IN THE SYNTHESIS AND DESIGN OF TAP COMPLEXES

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Abstract. Halogenated 1,3,5-triazapentadiene (TAP) complexes have emerged as an important class of coordination compounds due to their structural diversity, tunable electronic properties, and ability to participate in directed noncovalent interactions. This review summarizes the role of halogen bonding in the synthesis, structural organization, and functional design of TAP-based metal complexes. Particular attention is given to the theoretical background of halogen bonding, including the σ-hole concept and the directional nature of C–X···Lewis base interactions. The main synthetic approaches to TAP complexes are discussed, including complexation of preformed TAP ligands, metal-templated condensation reactions, and solvothermal methods. The review also highlights how coordination bonds, hydrogen bonds, and halogen bonds act cooperatively to stabilize molecular and supramolecular architectures. Structural studies of Mn, Fe, Co, Ni, Cu, Zn, and Pd complexes demonstrate that halogen bonding can influence crystal packing, metal-dependent Cl···Cl contacts, Pd···Cl interactions, and the formation of extended networks. Computational approaches, including molecular electrostatic potential analysis, QTAIM, NCI, and NBO calculations, further support the importance of these interactions. The functional relevance of TAP complexes in catalysis, crystal engineering, supramolecular chemistry, and the development of functional materials is also discussed. Overall, halogen bonding is shown to be a powerful tool for controlling the synthesis, stability, and supramolecular design of TAP complexes.

Keywords: halogen bonding; TAP complexes; 1,3,5-triazapentadiene; coordination chemistry; supramolecular chemistry; crystal engineering; noncovalent interactions; σ-hole; metal-templated synthesis; functional materials.