Two-Dimensional Inorganic Cationic Network of Thorium Iodate Chloride with Unique Halogen-Halogen Bonds

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A robust cationic network material featured with trigonal-pyramidal halogen bond geometries was obtained. ThIOCl is a rare example of a pure inorganic cationic material constructed from halogen−halogen bonds. All chloride anions are trapped by multiple strong halogen-halogen interactions with short Cl-I bond lengths ranging from 3.134 to 3.333 Å, forming a special Cl-centered trigonal pyramid polyhedron as a newly observed coordination mode for halogen bonds. Density functional theory (DFT) calculations clarified that electron transformed from central Cl atoms to I atoms generating a halogen-halogen interaction energy with a value of about -8.3 kcal/mol per Cl⋯I pairs as well as providing a total value of -57.9 kcal/mol among delocalized halogen-halogen bonds, which is a new record value reported for a single halogen atom. Additional hydrogen bond interaction is also present between Cl⋯OH and the interaction energy is predicted to be -8.1 kcal/mol, confirming the strong total interaction to lock the interlayer Cl anions. The present work demonstrated a new strategy in the combining of weak coordinated anions and weak interaction to synthesize inorganic cationic materials.

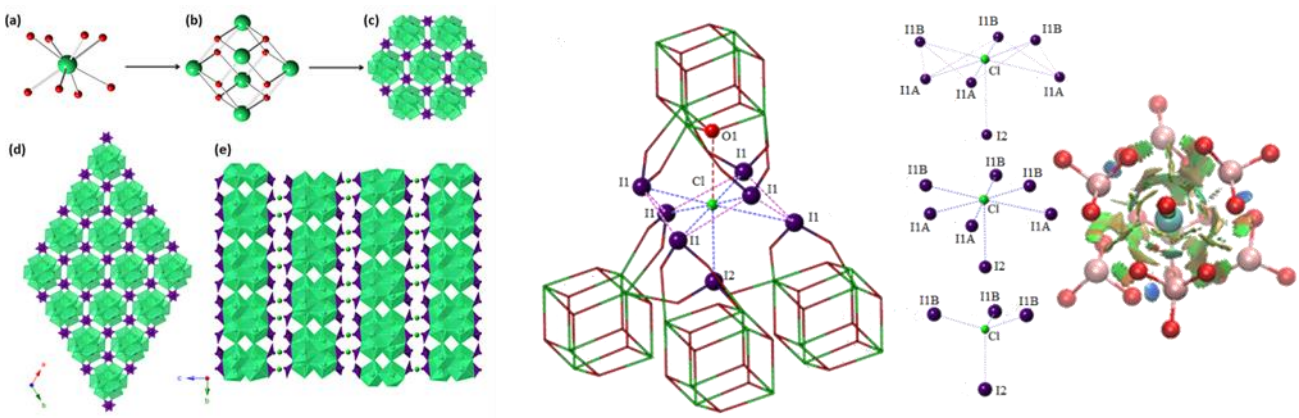

Fig.1. Structures and fragment models of **ThIOCl** in the 3D framework.

REFERENCES

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