

FROM SEMICOORDINATION TO METAL-INVOLVING HALOGEN BONDING IN ADDUCTS OF SQUARE PLANAR DITHIOCARBAMATES WITH *sym*-TRIIODOTRIFLUOROBENZENE

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Metallophilic interactions [1], R–H⋯M hydrogen bonding [2], and semi-coordination bonding [3] are widely investigated metal-involving noncovalent interactions. In cases of polar $M^{\delta+}\cdots M^{\delta-}$ metallophilic interactions and hydrogen bonding metal centers can be nucleophilic partners. The nucleophilicity of such metal centers as Ni^{II} , Pd^{II} , and Pt^{II} is provided by their sterically available d_{z^2} orbitals. Recently, the metal-involving halogen bonding were found [4–7], where these metal centers are nucleophiles toward covalently bound halogen atoms as σ -hole electrophiles [8].

In this work, we describe the rare C–I⋯M interactions between metal centers in square planar dithiocarbamates $[M(Et_2NCS_2)_2]$ ($M=Cu^{II}$, Ni^{II} , Pd^{II} , Pt^{II}) and iodine atoms of *sym*-triiodotrifluorobenzene (FIB) (Fig. 1), which were found in their isomorphous 1 : 2 adducts investigated by single-crystal X-ray diffraction experiments.

In all cases, the C–I⋯M contacts are followed by the C–I⋯S halogen bonding (Fig. 2). Accordingly to further theoretical calculations (Fig. 3), the nature of metal-involving interaction changes from semicoordination in case of electrophilic Cu^{II} to halogen bonding with nucleophilic Ni^{II} , Pd^{II} and Pt^{II} centers. Due to isomorphism of four adducts, other crystal packing effects are almost similar, and the differences between the C–I⋯M interactions can be correlated with the differences between metal centers.

We believe these new metal-involving interactions can be important in supramolecular chemistry and in the mechanistic studies of metal-involving reactions.

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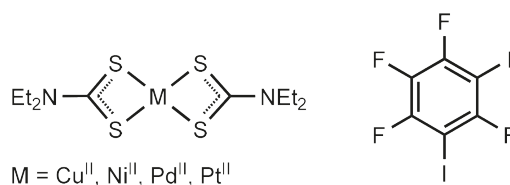


Fig. 1. Structures of compounds under consideration

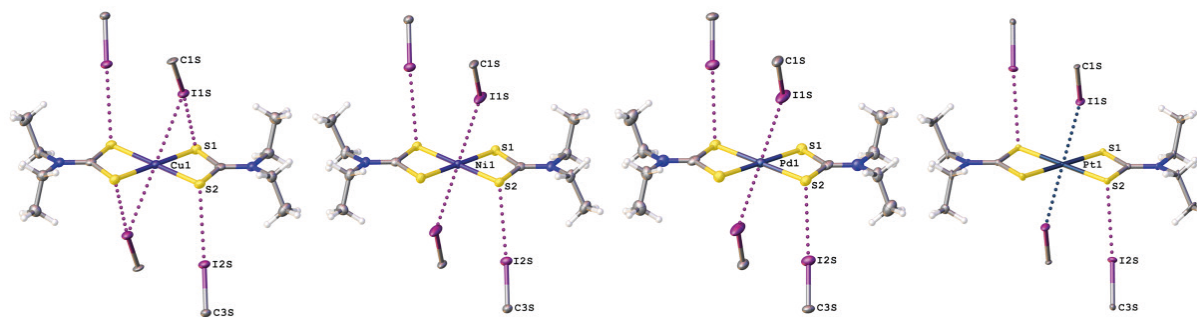


Fig. 2. Noncovalent interactions found in $[M(Et_2NCS_2)_2] \cdot 2FIB$. Only C–I fragments of FIB were left for clarity

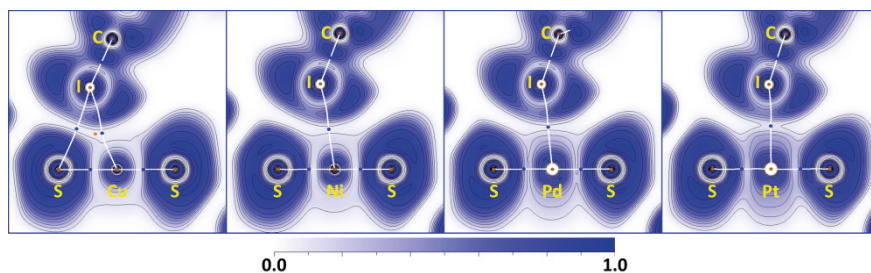


Fig. 3. The electron localization function projections of the C–I...M interactions

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DESIGN OF NEW SUPRAMOLECULAR COORDINATION CAGES BASED ON TETRASULFONYLCALIX[4]ARENES IN THE CRYSTALLINE PHASE

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Tetrasulfonylcalix[4]arene (SO₂C[4]A) in the cone stereoisomeric form, due to the presence of closely disposed donor oxygen atoms (Fig. 1) (from OH groups both with SO₂-bridges), are attractive polydentate ligands and are widely used as molecular building blocks for the construction of new polynuclear supramolecular discrete or polymeric coordination compounds [1, 2]. In particular, the involving of polytopic auxiliary ligands bearing

carboxylic binding sites in coordination with *in situ* generated *d*-clusters based on sulfonylcalix[4]arene may lead to formation of porous discrete entities, called supramolecular coordination cages, possessing of different attractive functions (gas/liquid storage, separation, traps for highly reactive particles, nanoreactors, catalysis, especially, photocatalysis, etc.) [3, 4].