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BOOK OF ABSTRACTS

METAL-INVOLVING NONCOVALENT INTERACTIONS IN PLATINUM(II) DITHIOCARBAMATE COMPLEXES

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In the past five years, the demand for square-planar d^8-metal complexes as sterically accessible sites involved in diverse noncovalent interactions (NCI) has increased dramatically. Despite their positive charges, these centers can function as d_z^2-orbital centered nucleophiles toward various σ- and π-hole donors. According to our previous experience a substantial increase of d_z^2-nucleophilicity can be achieved by employing strong electron-donating dithiocarbamate ligands [1-2]. Thus, Pt(II) dithiocarbamate complexes have been previously employed by us as multifunctional NCI acceptors: $[Pt(S_2CNEt_2)_2]$ was stacked with electron-deficient arenes via $\{d_z^2\text{-}Pt^{II}S4\}\cdots$π-hole interactions [1], and also formed $I\cdots Pt^{II}$ halogen bonds with perfluorinated iodoarenes [2].

These studies stimulated our further interest in relevant systems and for the continuation of our project we addressed Pt(II) dithiocarbamates bearing mixed chelating ligands – $[Pt(PPy)(S_2CN(CH_2)_n)]$ (PPy – 2-phenylpyridine; n = 4 (**1**), 6 (**2**)). The complexes **1** and **2** were co-crystallized with tellurides $TePy^F{}_2$ (Py^F = C_5F_4N-4) and $TeTol^F{}_2$ (Tol^F = $C_6F_4CF_3$-4) to form cocrystals **1**·$TePy^F{}_2$, **2**·$TePy^F{}_2$, and **2**·$TeTol^F{}_2$, whose structures were studied by single-crystal X-ray diffraction (XRD). In all three structures, we observed stacking interactions between the complexes and the tellurides, which involve a few types of NCI (Fig. 1). The stacking includes contacts between a metal center and Te and/or an arene of $TeR^{EWG}{}_2$. In the cocrystals, several atoms exhibit NCI acceptor abilities: Pt center, S-atom of the dithiocarbamate ligand, and a C-atom of the ppy ligand are involved in chalcogen bond with Te; the phenyl ring of the ppy ligand, C-atom of the dithiocarbamate, Pt donate electron density to π-holes of the Py^F (or Tol^F) groups. The multiplicity of NCI centers in each of the coformers leads to a diversity of the formed noncovalent contacts.

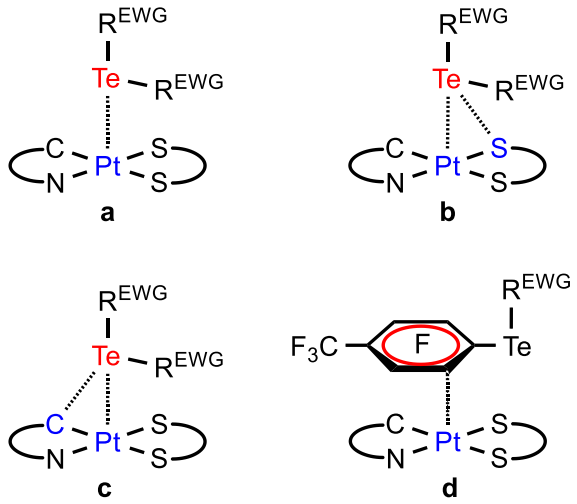

Figure 1. Identified metal-involving contacts.

Our DFT analysis using QTAIM, NCIPlot, and NBO methods has elucidated the complex interplay of NCI within the cocrystals. These studies have highlighted the presence of significant chalcogen bonds, lone pair interactions, and π-stacking, all contributing to the stability of the dimeric assemblies. This research enhances our understanding of NCI and provides a foundation for the development of new materials leveraging these intricate chalcogen bond interactions.

References

[1] *Inorg. Chem. Front.* **2022**, *9*, 2869
[2] *Inorg. Chem. Front.* **2021**, *8(10)*, 2505