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## **1,2,5-chalcogenadiazoles – donors of chalcogen bonding for molecular recognition and sensorics**

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1,2,5-chalcogenadiazoles – a class of heterocyclic compounds with interesting set of inherent properties, most notably the  $\pi$ -acceptor properties due to the electron deficiency of the heterocyclic system and therefore high electron affinity. As  $\pi$ -acceptors these compounds are used for the preparation of radical-anion salts, charge transfer complexes and building blocks for polyconjugated organic semiconductor materials.

At the same time these compounds display  $\sigma$ -acceptor properties, forming supramolecular complexes with Lewis bases (LB), which are coordinated to the chalcogen atom via chalcogen bonding – a secondary bonding interaction between lone electron pair of LB and a region of depleted electron density with a local positive electrostatic potential – a  $\sigma$ -hole. These  $\sigma$ -hole may be visualized via the DFT calculation of the map of electrostatic potential on the isoelectronic surface (MEP). Figure 1 depicts a scheme of the chalcogen bonded complex formation, as well as an example of such a complex together with the molecular electrostatic potential map of the recently studied 5,6-dicyano[1,2,5]selenadiazolo[3,4-*c*]pyrazine. It should be noted that MEP only provides information on the electrostatics of the free molecule, while the chalcogen bonding energy is a sum of electrostatic, orbital and dispersion interactions energies, and for various chalcogen bond donors these contributions can significantly vary. Particularly, calculations for the halide complexes of **1** demonstrate that the largest contribution to the bonding energies come from electrostatic and dispersion interactions, while previously complexes of structurally related 3,4-dicyano-1,2,5-chalcogenadiazoles were mostly formed via orbital interactions.

Complexes are isolated and their crystal structures are determined via XRD. Notably the chalcogen bond has a strong directionality as LBs are always located near the plane of the heterocycle and on the extension of the N-E bond. Upon complexation a new long wave-length charge transfer band appears in the electronic absorption spectra. This spectral change is used for spectrophotometric determination of complex formation constants. Complexes have a wide range of formation constants depending on the nature of the heterocycle and LB. Particularly, Te heterocycles possess the largest  $\sigma$ -holes and therefore build stronger complexes than Se and S congeners. Additionally, electronegative atoms, such as N atoms of pyrazine ring and electron withdrawing groups, such as cyano groups in the backbone of the molecule enhance the ability to form chalcogen-bonded complexes. This allows to fine tune the coordinating ability via molecular design of the receptor. On the other hand the spectral change may be used as an analytical signal for the sensing of certain LBs. This contribution discusses synthesis, structure, thermodynamic and optical properties of these complexes relevant for the possible applications of chalcogenadiazoles as receptors and sensors.