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Recognition and sensing of Lewis bases by 1,2,5-chalcogenadiazoles

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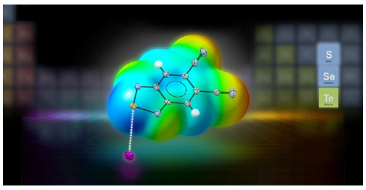
Chalcogen bonding-driven interaction of 1,2,5-chalcogenadiazoles with charged and neutral Lewis bases is discussed. It is highlighted that this interaction is a promising method for optically-detected recognition and sensing of the bases, and, at one, for the formation of otherwise challenging chemical bonds.



Keywords: 1,2,5-chalcogenadiazoles, chalcogen bonding, chemical recognition and sensing, Lewis bases, noncovalent interactions, secondary bonding interactions.

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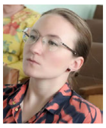

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Introduction

Molecular recognition[1] is a specific host–guest complexation[2] of two or more chemical entities driven by secondary bonding interactions[3] (SBIs; aka noncovalent or unorthodox interactions).[†,4] It is vital for fundamental chemistry; and its applications span across materials, catalysis, life and environment sciences,[4–7] as well as public security.[8] When $[\mathrm{A}]^{n-}$ anions or $[\mathrm{Cat}]^{n+}$ cations are involved, it is termed ion recognition; in solutions, solvents also participate and frequently their effects are substantial.[‡,9] The recognition of $[\mathrm{A}]^{n-}$ is more challenging than that of $[\mathrm{Cat}]^{n+}$. Stereoelectronic properties of $[\mathrm{A}]^{n-}$ are widely varied; spatially, they are larger than relevant $[\mathrm{Cat}]^{n+}$ with, therefore, lower charge-to-size ratios. Normally, $[\mathrm{A}]^{n-}$ have high solvation energy. These factors interfere with the host–guest interactions embracing $[\mathrm{A}]^{n-}$.[3(*d*),5(*c*),(*d*)–(*f*),6,10,11]

Frequently, the molecular/anion (hereinafter, chemical) recognition is accompanied by response in electronic adsorption (VIS) or/and emission (FL) spectra enabling optical sensing;[10(*a*),12] with $[\mathrm{A}]^{n-}$, it resembles their well-established spectrophotometric determination in analytical chemistry.[13] Combination of $[\mathrm{A}]^{n-}$- and $[\mathrm{Cat}]^{n+}$-targeting moieties in a single scaffold allows cooperative ion-pair recognition/sensing.[11(*b*),14] The design, synthesis and functional characterization of new artificial receptors/chemosensors, together with elaboration of relevant experimental/theoretical methods, is a hot topic wherein various SBIs (*e.g*. hydrogen bonding *HB*, *etc*.)[3(*d*),10(*a*),15–17] are actively exploited.[§,18]

1,2,5-Chalcogenadiazoles (unless otherwise indicated, chalcogen E = S, Se, Te) and their fused derivatives are heteroaromatic chromogenes (VIS)/fluorogenes (FL)[¶] and Lewis ambiphiles[19,20(*a*),21(*a*),22] whose ambiphilicity is dual in the sense that both σ- and π-MOs are involved in both acidic and basic behaviour.[19(*b*)] Due to this, their molecules, as well as related 1,2,5-chalcogenadiazolium cations, function as mutual receptors: in the solid state,[23–28] solution,[29] and gas phase[30] they are aggregated by $[\mathrm{E{-}N}]_n$ (n = 1, 2) specific SBI termed chalcogen bonding (*ChB*, see below).[31] At the beginning of 2010s,[††,32] it was discovered that 1,2,5-chalcogenadiazoles acting as Lewis acids are unimolecular receptors and sensors of charged[33] and neutral[25(*c*),34(*b*)] Lewis bases (*i.e.*, $[\mathrm{A}]^{n-}$ and LBs, respectively).[‡‡,17(*e*),(*f*),19(*a*)–(*c*)] Later on, it was realized that this interaction is *ChB*-driven and possesses the general character.[19(*b*),34] It was also found that the *ChB* formation is accompanied by charge transfer (CT)[§§,3(*b*),35] from $[\mathrm{A}]^{n-}$/LB guests onto chalcogenadiazole hosts. The CT, being more pronounced with $[\mathrm{A}]^{n-}$, manifests itself in a new band in VIS spectra,[25(*c*),33] thus enabling sensing. Besides, *ChB* is redox-switchable and this can also be used in recognition/sensing.[36]

Apparently, the cyclic/heteroaromatic structure of 1,2,5-chalcogenadiazoles[20(*a*),37] is important for LB recognition/sensing. The *a priori* potential of their $(\mathrm{R{-}N{=}})_2\mathrm{E}$ acyclic analogues to form *ChB* is markedly lower: reported reactions with $[\mathrm{A}]^{-}$ proceed as π-addition,[20] whereas complexes with neutral LBs are unknown (ESM).

The *ChB*-driven chemical recognition/sensing by 1,2,5-chalcogenadiazoles, as well as by other *ChB* donors,[17(*b*)] is promising for further research. The fast-growing relevant information is, however, scattered. To encourage and facilitate the research, here we discuss fundamentals, applications and prospects of complexation of 1,2,5-chalcogenadiazoles with neutral and charged LBs by means of *ChB*. Complexation with π-LBs,[29(*b*),38,39] *e.g.* with various TTFs by π-stacking interactions instead of *ChB*, is not encompassed. Besides the recognition/sensing itself, involved reactions assemble otherwise hardly accessible chemical bonds, *e.g*. between different E atoms.

1,2,5-Chalcogenadiazole receptors/sensors where (1) non-*ChB* (*e.g. HB*) SBIs are employed,[18(*b*),40] or (2) preliminary guests reactions with pro-hosts leading to the *in situ* formation of actual receptors/sensors are necessary,[21] are not discussed since chalcogenadiazole cores do not directly participate in the host–guest binding and function only for VIS/FL response. Out of consideration are also 1,2,5-chalcogenadiazolium salts and their complexes with neutral parent molecules displaying *ChBs* in the solid state.[25(*a*),26(*a*),41] As LBs, 1,2,5-chalcogenadiazoles form coordination compounds, including FL ones,[42] with such Lewis acids as metal $[\mathrm{Cat}]^{n+}$ and can be used in their reception/sensing.[¶¶,18(*b*),43] This, however, requires special consideration.

Chalcogen bonding

By the IUPAC definition, *ChB* is a net attractive interaction between an electrophilic region associated with an E atom in a molecular entity and a nucleophilic region in another, or the same, molecular entity.[31] Additionally, a *ChB* formed by the E···E pair interactions, in which each E atom serves as an electron donor in one interaction and acceptor in another, is discussed.[44] As any chemical bond, *ChB* is not a physical observable[45] and can be discussed only by means of various descriptors. For theoretical analysis of *ChB*, those from MEP, QTAIM, NCI, EDD, SAPT, NBO, EDA and some other quantum chemical tools[†††,17(*h*),46] are especially useful with DFT or/and post-HF

[†] By definition, SBIs are interactions resulting in interatomic contacts that are longer than covalent single bonds (*i.e.*, the sum of the corresponding covalent radii) but shorter than the sum of the corresponding van der Waals (VdW) radii. Widely used term *noncovalent interactions* is misleading since it does not specify the interaction character, *i.e.*, attractive or repulsive, and covers only electrostatic and dispersion interactions in the situations where covalent interactions/orbital overlap cannot be neglected.

[‡] In this aspect, ion recognition in solution relates to an emerging research discipline termed ioliomics and focused on studying ions in liquids.

[§] Amongst others, abiotic arene-polyfluoroarene π-stacking SBI is promising for biomedicine; however, it is less studied in this context.

[¶] Currently, FL/VIS properties of 1,2,5-chalcogenadiazole (chalcogen = S, Se) dyes are widely used in bioimaging (including super-resolution imaging) and organic electronics. Some derivatives reveal solvato-, thermo-, and/or mechanochromism; and heavy-atom containing ones, phosphorescence. Some of the dyes are promising for *ChB*-based molecular recognition.

[††] Actually, the first *ChB*-bonded chalcogenadiazole complex [**4**–Cl]$^{-}$ (Figure 2; CCDC 644965) was synthesized in 2007 but the Se–Cl *ChB* was overlooked due to its distance exceeding the sum of covalent radii of the partners.

[‡‡] Lewis ambiphilicity of the title compounds enables forming complexes also with Lewis acids, *e.g.* with $\mathrm{R_3B}$; when R = Hal, the complexes feature intramolecular *ChBs*.

[§§] Despite criticism from physics, CT is widespread useful descriptor in chemistry.

[¶¶] In some real $[\mathrm{Cat}]^{+}$ receptors/sensors, chalcogenadiazole core may be not directly involved in SBIs-based binding; or may be as N-donor ligand. In both cases, it serves for VIS/FL response covering, particularly, NIR area.

[†††] The molecular electrostatic potential (MEP) theory, quantum theory of atoms in molecules (QTAIM), noncovalent interaction (NCI) index, electron density difference (EDD) analysis, and symmetry-adapted perturbation theory (SAPT) presumably deal with electron density ρ, which is a physical observable. The NCI overcomes limitations and fully utilizes the tools of QTAIM caused by local character of its descriptors; particularly, NCI represents SBIs as continuous surfaces rather than close contacts (bond critical points) between atom pairs. The EDD clarifies CT, and the SAPT discloses the inherent nature of SBIs including dispersion interactions. In natural bond orbital (NBO) method, the wavefunction is transformed into a localized set of natural bond orbitals, which are an intermediate between the basis AOs and the canonical MOs; NBO allows

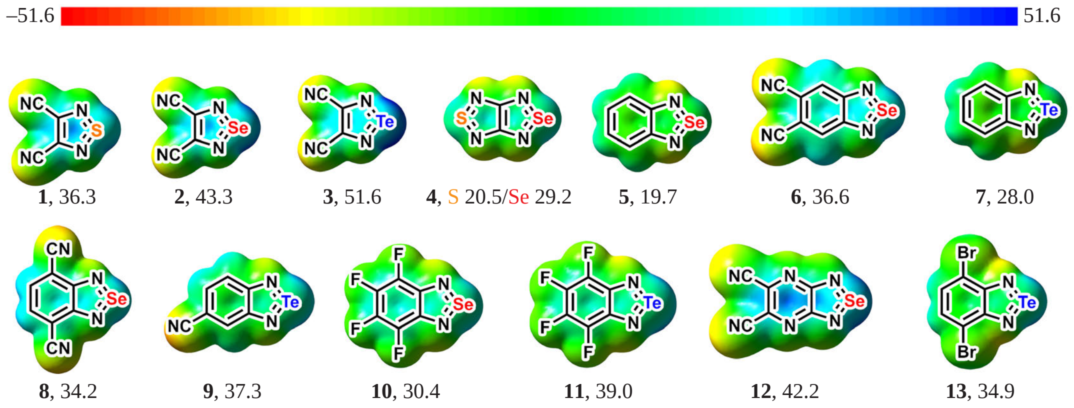

Figure 1 B3LYP/def2-tzvp-calculated MEPs of chalcogenadiazoles **1**–**13** (0.001 e Bohr^{-3} isosurface) featuring σ- and π-holes, together with $V_{\mathrm{S,max}}$ (kcal mol^{-1}) of the σ-holes.

calculations in the background. Despite criticism,[47] the QTAIM topological descriptors, *e.g*. bond/line[47(b)] critical points (bcp's), are instrumental and included in the IUPAC's *ChB* list of features. For experimental study, such techniques as XRD,[15(b),23(a),24(a),25(a)–(c),26(g),(h),29(a),48] solution and solid-state VIS/FL[24(a),33(a),34(a)–(d),49] and NMR,[17(e),34(b),(c),50] ESI-MS,[29(a),33(b),34(b),(c)] and IR/Raman[34(b),50(e),(f),51] are mainly exploited;[‡‡‡] *ChB* assessment in solution is sometimes challenging.[24(b),49] Also useful is data mining, *e.g*. in the Cambridge Structural Database,[52] applied to validating the assumptions used in experimental/theoretical studies of *ChB* and evaluating/categorizing its strength; the mining, particularly, evidences the *ChB* strengthening with the increase in the polarizability of the E atom (Te > Se > S) and places *ChB* operating distances in the ranges 2.4–*n* Å (*n* = 3.6, 3.8, and 4.1 for E = S, Se, and Te, respectively).[53]

For *ChB*, both enthalpy and entropy of the formation are important. Affinity and selectivity of *ChB* are controlled by subtle interplay involving host, guest and solvent; especially, when the solvent is LB capable of *ChB*, *e.g*. THF.[54] As a stereoelectronic entity, *ChB* is a balance of attractive electrostatic, orbital, and dispersion interactions and repulsive Pauli/steric interaction.[23(a),26(c),55] The electrostatic interaction is associated with electrophilic areas at atoms in molecules. In MEP theory, such areas arising from the anisotropy of the atomic charge distributions and corresponding to MEP positive values are termed σ- and π-holes.[17(h),46(a),(b)] The σ-holes, visualized with Kelvin probe force microscopy,[17(i)] are spatially located on the outer extensions of the σ-bonds, and π-holes are positioned above and below the molecular plane (for selected title compounds **1**–**13**, see Figure 1). The presence of unshared electron pairs at the π-hole's central atom attenuates the hole and shifts its position; it results in the weakening of the π-hole and the hole-based SBIs.[56] The holes can be quantified by the magnitudes of the corresponding MEP maxima $V_{\mathrm{S,max}}$, within the HSAB concept[57] characterizing the hard nature of the *ChB*; whereas the Fukui function[58] can be used for characterizing both hard and soft nature.[59] An inherent part of electrostatic interaction is polarization; for weak interactions such as SBIs, polarization is equivalent to CT with a difference that the former is the physical observable and the latter only theoretical/computational model.[§§,3(b),45]

In chemical recognition/sensing with 1,2,5-chalcogenadiazoles, σ-holes are mainly involved;[17(j),55(a),60] simultaneous participation of both σ-holes at the same E atom is possible.[29(a),33(b),34(a),61] All else being equal, $V_{\mathrm{S,max}}$ magnitude/*ChB* strength enlarges in the order S < Se < Te[26(i),34(c),59] (*cf*. compounds **1**–**3**, **4** with two different E atoms, **5** and **7**, and **10** and **11**; Figure 1), *i.e*., with enlarging polarizability of the E atoms.[62] For 6–5 fused incarnations, the magnitudes can be modulated by substitution in the six-membered cycle or/and $\mathrm{N^+}$–R quaternization/N→O oxidation in the five-membered one. When it lowers molecular symmetry from C_{2v}, σ-holes become nonequivalent.[24(b),25(a),26(a),(i),34(c),63] With π-basic guests, the *ChB* can be formed by σ-hole-based E···π interactions.[19(d),50(d)] With sterically inaccessible σ-holes, π-hole-driven *ChB* is observed.[64]

Orbital contribution into *ChB* corresponds to the Alcock model.[3(a)] With chalcogenadiazole host, it is an overlap of virtual σ*-MO of its E–N bond with unshared *n*-MO of the guest accompanied by *n*→σ* CT, *i.e*., by negative hyperconjugation;[65] or, rarely, by π→σ* CT as with the $[\mathrm{Ph_4B}]^-$ guest.[19(d)] If a π-hole is involved, whose peculiarity is enhanced amplitude of the π*-MO in the hole area, a better overlap with the *n*-MO leads to a bigger *n*→π* CT.[56] The orbital contribution/CT connects *ChB* with a more common donor–acceptor coordinate bond.[66] Together with electrostatic contribution, the orbital one is responsible for the covalency/directionality of *ChB*.[17(j),59,61(c),67] With SAPT[†††] calculations on relevant 1,3-tellurazoles, however, it was found that Pauli repulsion/steric interaction is more important for the *ChB* spatial orientation[68] highlighting once again the maverick situation of Te amongst the chalcogens.[69] Dispersion[70] contribution into *ChB* is linked with higher atomic polarizability of heavier atoms[62] in the hosts/guests (*e.g*. Se, Te/$[\mathrm{Br}]^-$, $[\mathrm{I}]^-$).

Similar to SBIs in general, the real or potential significance of *ChB* covers not only fundamental and applied chemistry but also biomedicine (*e.g*. drug design) and materials, catalysis, separation and environmental sciences.[17(e),(g),26(i),55(c),61(c),67(a),71,72]

Anions

As $[\mathrm{A}]^{n-}$ receptors/sensors in solutions, compounds **1**–**13** are studied (Figure 1, Scheme 1).[24(a),32,33(a),(b),34(a)–(e),35,43(d),73] Unlike other $[\mathrm{A}]^-$, $[\mathrm{CN}]^-$ and $[\mathrm{ECN}]^-$ (E = O, S, Se, Te) possess two different coordination sites and reveal an ambivalent

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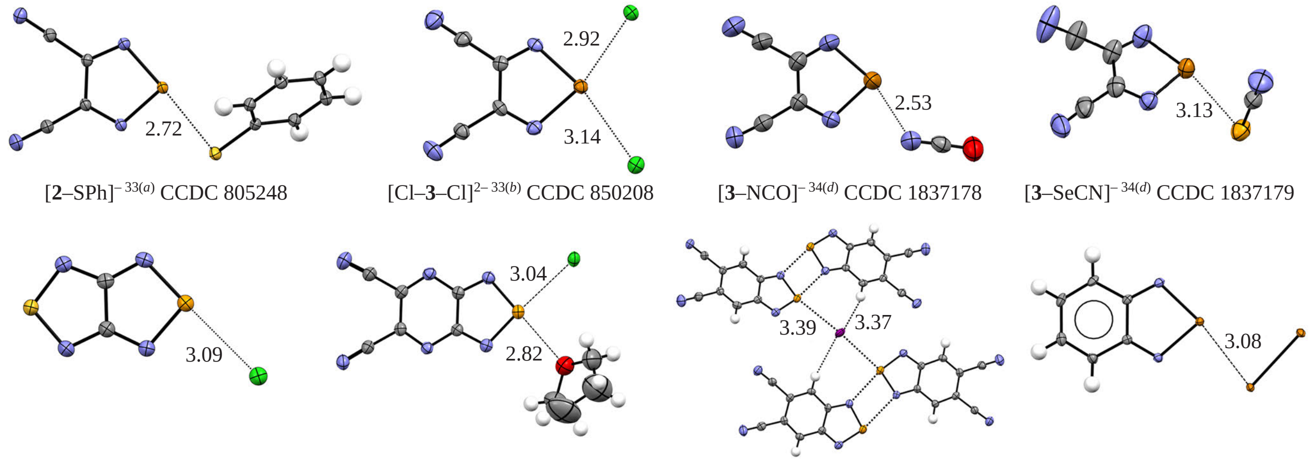
using of such chemical concepts as Lewis structures, charge and CT, bond type and order, *etc*. The energy decomposition analysis (EDA), which can be performed with SAPT, partitions the interaction energy into electrostatic, exchange (*i.e*., Pauli repulsion), induction (*i.e*., orbital) and dispersion contributions; combined with natural orbitals for chemical valence approach (EDA-NOCV), it provides further dividing energy of orbital interaction into pairwise contributions of the most relevant MOs.

[‡‡‡] Amongst spectral methods, still unemployed in the field resonance Raman (RR) spectroscopy (enabling structural identification of *ChB*-relevant CT chromophores with very high sensitivity) and nuclear quadrupole resonance (NQR; ~50% of chemical elements have quadrupole nuclei) are promising.

F^- Cl^- Br^- I^- NO_2^- CN^- OCN^- SCN^- $SeCN^-$ $TeCN^-$
HSO_4^- $H_2PO_4^-$ CH_3COO^- $CF_3SO_2O^-$ PhS^- $PhTe^-$ SO_4^{2-} CO_3^{2-} **7**$_2^-$ PO_4^{3-}
$^-$Te–Te$^-$ $^-$Te–Te–Te–Te$^-$

Scheme 1 Anions studied with chalcogenadiazoles **1**–**13**.



[**2**–SPh]$^-$ [33(a)] CCDC 805248 [Cl–**3**–Cl]$^{2-}$ [33(b)] CCDC 850208 [**3**–NCO]$^-$ [34(d)] CCDC 1837178 [**3**–SeCN]$^-$ [34(d)] CCDC 1837179

[**4**–Cl]$^-$ [32] CCDC 644965 [Cl–**12**–THF]$^-$ [73(a)] CCDC 2168136 [**6**$_4$–I]$^-$ [24(a)] CCDC 2241712 [**7**$_4$–Te$_2$]$^{2-}$ [34(e)] CCDC 1846535

Figure 2 Representative XRD structures of anionic complexes (ESM). The *ChBs* are indicated by dashed lines with bonds distances in Å. Colour code: C – grey, H – light gray, Cl – green, I – purple, N – blue, O – red, S – yellow, Se – golden yellow, Te – orange. Omitted [Cat]$^+$: [K(18-crown-6)]$^+$ for [**2**–SPh]$^-$, [**3**–NCO]$^-$, [**3**–SeCN]$^-$ and [**7**–Te$_2$]$^{2-}$; [PyH]$^+$ for [Cl–**3**–Cl]$^{2-}$; [Et$_4$N]$^+$ for [**6**$_4$–I]$^-$ and [Cl–**12**–THF]$^-$.

reactivity contradicting to HSAB concept.[57,74] The formation of the complexes is usually confirmed by VIS spectroscopy combined with TD-DFT and/or NBO calculations, and ESI-MS ([**3**–A]$^-$ (A = F, Cl, Br, I, PhS), [**13**–Cl]$^-$)[33(b),34(b),(c)] and multinuclear NMR ([**3**–F]$^-$) techniques.[34(b)]

Numerous *ChB*-bonded [A]$^{n-}$ (n = 1, 2) complexes were isolated in the form of salts with various [Cat]$^+$ and characterized by XRD (Figure 2; ESM), solid-state UV–VIS and NMR, and quantum chemical calculations. Complexes with 1 : 1, 1 : 2, 2 : 1 and 4 : 1 stoichiometry were observed; for [**3**–Br]$^-$, polymorphs were found. The structures depend on [Cat]$^+$; the [A]$^{n-}$ function as both mono- (most cases) and ditopic/bridging ([**7**–Te$_4$–**7**]$^{2-}$, [**12**$_2$–Cl]$^-$) ligands. The 1 : 2 complexes highlight the presence of two σ-holes at the E atoms and feature bifurcate *ChB*; some of them are heteroleptic, *e.g.* simultaneously containing [A]$^-$ and LB ligands as [Cl–**12**–THF]$^-$ (Figure 2). The bifurcate *ChB* with bridging [A]$^-$ is also observed for 1 : 1 complexes with [PyH]$^+$, [Et$_4$N]$^+$, [Bu$_4$N]$^+$ and [R$_4$P]$^+$ (R = Ph, Et) counter cations; the structures feature [M–A]$_2^-$ dimers (M = **2**, **3**, **12**; A = Cl, Br, I).[33(b),50(c),(d),73(a)] With **6**, complexes [**6**$_4$–A]$^-$ were isolated from reaction solutions presumably containing [**6**–A]$^-$ (A = Cl, Br, I; see below). Their 4 : 1 structure with clustering of **6** around [A]$^-$ (*e.g.* [**6**$_4$–I]$^-$, see Figure 2) is caused by a cooperativity of *ChB* and *HB*. The latter is crucially important since isomeric **8**, incapable of simultaneous coordination of [A]$^-$ by *HB* and *ChB*, does not form isolable complexes under the same conditions. Furthermore, in the crystal, [**6**$_4$–A]$^-$ are connected by the π-hole-driven *ChB*; overall, each [A]$^-$ is six-coordinated. Tetra- and pentafurcate *ChB* is observed for 2 : 1 complex [**12**$_2$–Cl]$^-$.[24(a),32,33(a),(b),34(a)–(e),73(a)] Some complexes were not isolated and characterized by solution VIS spectra and/or quantum chemical calculations.[17(d),34(c),59,61(b),75]

The common structural peculiarity of all studied real/putative complexes is that the *ChB* is longer than the sum of the covalent radii[76(a)] of the involved atoms but shorter than the sum of their VdW radii;[76(b)] and the difference between the sum of VdW radii of interacting atoms and the *ChB* experimental distance is a descriptor of the *ChB* strength. The NBO/NOCV analyses suggest that an interaction of the *n*-MO of [A]$^-$ (*i.e.*, *p*-AO) with the E–N σ*-MO of chalcogenadiazole (Figure 3) specifies orbital contribution in the *ChB* (*i.e.*, its covalency) and the *n*→σ* character of the CT.[17(d),24(a),32,33(a),(b),34(a)–(e),59,61(b),67(a),73(a),(b),75]

The CT manifests itself in new bands/shoulders in the solution and solid-state VIS spectra of [M–A]$^{n-}$, which are red-shifted as compared with the longest-wavelength bands in spectra of the parent M. In MeCN, λ_{max} (hereinafter, in nm) of these bands/shoulders are ~400 for [**3**–SeCN]$^-$, and ~450–460 for [M–SPh]$^-$ (M = **2**, **3**) and [**6**$_4$–I]$^-$.[24(a),33(a),34(a),(b),(d)] For [**12**–A]$^-$ in THF/MeCN, λ_{max} is 436/405 (shoulder, 450) (A = Cl), and 496/488 (A = Br); with A = I, the band is shifted to ~600 (tail extends into NIR region). The variation of VIS spectra of [**12**–A]$^-$ in these solvents implies structural reorganization or/and specific solvation.[73(a)] The solid-state VIS spectra of complexes are broadened as compared with solution ones, but the bands' maxima coincide fairly well providing XRD-based structural ideas for solutions.[73(a)] With **6**, however, solution VIS spectra of **6** + [Et$_4$N]$^+$[A]$^-$ (A = Cl, Br, I) reaction mixtures are markedly different from the solid-state spectra of the isolated [Et$_4$N]$^+$[**6**$_4$–A]$^-$ (whereas variable-temperature ^{35}Cl and ^{77}Se NMR spectra are less informative); thus, for [Et$_4$N]$^+$[**6**$_4$–I]$^-$ λ_{max} is shifted from ~460 to ~600. Dissolved in MeCN, the authentic

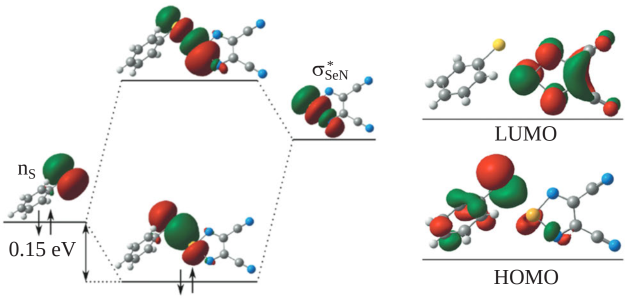


Figure 3 Left: the formation of the Se–S *ChB* of [**2**–SPh]$^-$ in the **2** + [PhS]$^-$ reaction. Right: the frontier MOs of [**2**–SPh]$^-$ involved in the lowest-energy electronic transition corresponding to the CT band in its VIS spectrum. Adapted with permission from ref. 33(*a*); copyright 2011 American Chemical Society.

[Et$_4$N]$^+$[**6**$_4$–A]$^-$ reproduce VIS spectra of the **6** + [Et$_4$N]$^+$[A]$^-$ reaction mixtures implying the formation of the [**6**$_4$–A]$^-$ during the crystallization of the [Et$_4$N]$^+$[**6**$_4$–A]$^-$.[24(a)]

For [M–A]$^-$ (M = chalcogenadiazole, *e.g.* **3**), NBO suggests that the electronic transitions responsible for the CT bands involve the frontier MOs localized at M's different areas (see Figure 3).[33(a),34(a),(d)] For clustered [**6**$_4$–A]$^-$ (A = Cl, Br, I), the TD-DFT discloses that the excited states associated with CT transitions cannot be assigned to a single process of electron promotion from an occupied MO to a virtual MO but involve a number of the occupied MOs located mostly on A and the virtual MOs located mostly on **6**$_2$ pairs.[24(a)] Overall, the CT, numerically depending on the computational method, varies from low to moderate. The NBO/Mulliken CT (hereinafter, in e$^-$) is ~0.2–0.4/0.3–0.5 for [M–A]$^-$ (M = **1**–**3**; A = F, Cl, Br, I, CN, OCN, SCN, SeCN, SPh) and ~0.3/– for [**12**–A]$^-$ (A = Cl, Br, I); the highest Mulliken value of ~0.5 corresponds to [**3**–CN]$^-$.[33(a),34(a),(b),(d),73(a)] With NBO, CT of ~0.3 is the same for [**3**–Cl]$^-$ and [Cl–**3**–Cl]$^{2-}$.[33(b)] For [M–A]$^{n-}$ (M = **1**–**3**; *n* = 1, 2; A = F, Cl, Br, NO$_3$, SO$_4$), MP2-calculated CT varies between ~0.05 ([**1**–NO$_3$]$^-$) and ~0.3 ([**1**–SO$_4$]$^{2-}$).[61(b)]

Thermodynamic stability of complexes in solution and gas phase is different due to Gibbs free energy Δ*G* of solvation. For [M–A]$^-$ (M = **1**–**3**, **7**, **9**, **11**, **13**; A = F, Cl, Br, I) in THF, DFT suggests negative Δ*G* except [**1**–I]$^-$; for [**2**–I]$^-$, Δ*G* is negative but low, which corresponds to low association constant *K* (ESM). For [A–M–A]$^{2-}$, DFT predicts negative Δ*G* only for [A–**2**–F]$^{2-}$ and [A–**3**–A]$^{2-}$ (A = F, Cl, Br). According to XRD ([**3**–A]$^-$ and [A–**3**–A]$^{2-}$; A = Cl, Br) and DFT, coordination of the second [A]$^-$ always leads to the elongation of the *ChBs* due to the electrostatic repulsion.[33(b),34(a),(b)] The CT bands in VIS spectra allow experimental assessment of *K* and Δ*G* in solutions (ESM). In going from gas phase to solution, *K* decreases; the effect is much more pronounced in polar solvents. With various solvation models, DFT-calculated Δ*G* magnitudes reasonably agree with the experiment. Destabilization of the complexes in solution compared to the gas phase is associated with CT decrease, *e.g.* by 15–35% for [M–A]$^-$ (M = **1**–**3**) in THF; the same factor causes a higher destabilization in polar solvents compared to nonpolar. For example, *K* of [**3**–I]$^-$ in CH$_2$Cl$_2$ is 450 times higher than in MeCN; for [**2**–SPh]$^-$, the difference in Δ*G* is significantly smaller and *K* decreases by 25 times only (ESM).[33(a),(b),34(a),(b)] For [M–A]$^-$ (M = **7**, **9**, **11**, **13**), *K* in THF decreases in the A order Cl > Br > NO$_3$; the highest dispersion-corrected DFT-value of –Δ*G* is ~7 kcal mol^{-1} for A = Cl. For A = I, *K* is too small to be determined (ESM), or interaction is accompanied by the decomposition of M.[34(c)]

The electron-withdrawing substituents (*e.g.* F or CN)[§§§,17(k)] in six-membered cycles of 6–5 bicyclics considerably enlarge *ChB* donor ability (ESI) correlating with $V_{\mathrm{S,max}}$ at the E atoms[34(c)] In fluorocarbon series, **11** binds, and **10** does not bind, [A]$^-$ (A = F, Cl) *via ChB*. Related tetrafluoro 1,3-benzodiazole **14** coordinates [Cl]$^-$ *via HB* indicating that *HB* is more effective here for [A]$^-$ binding than *ChB*. This agrees with relative $V_{\mathrm{S,max}}$ magnitudes of **10**, **11** (see Figure 1) and **14** (60.2 kcal mol^{-1}) and suggests that selenadiazole–azole hybrids admitting *ChB* and *HB* cooperativity (*cf.* [**6**$_4$–A]$^-$) are promising for the field.[73(b)] Quantification of CT in [M–A]$^-$ and M–LB (M = 1,2,5-chalcogenadiazole) by charge-displacement (CD) analysis gives values linearly correlating (separately for [M–A]$^-$ and M–LB) with the experimental *K* in solution, thus allowing *a priori* evaluation of *K*.[75] Since CD analysis deals only with the CT/polarization (*i.e.*, orbital contribution in *ChB*), these correlations look as rather deterministic than stochastic and certifying the *ChB* covalency.

The pseudo halides do not interact with **1** and **2** due to unfavorable thermodynamics (ESM). Compound **3** and [K(18-crown-6)]$^+$[A]$^-$ in THF give [**3**−A]$^-$ (A = CN, NCO, SCN, SeCN) (see Figure 2; ESM); instead of [**3**−TeCN]$^-$, only unidentified products were obtained. Importantly, [CN]$^-$ did not provoke 1,2,5-chalcogenadiazole disintegration observed with charged C-nucleophiles.[77] In [**3**–A]$^-$, the softer side of [A]$^-$ is coordinated to the soft Te atom of **3**, which is thermodynamically favorable in both the gas phase and in solution (ESM).[34(d)] By contrast, **3** and [K]$^+$[SeCN]$^-$ in MeCN afforded [**3**–NCSe]$^-$ contradicting the DFT-calculated solution thermodynamics (ESM) probably due to the fact that the [Cat]$^+$ was not accounted. This highlights the role of [Cat]$^+$ hardness (*cf.* [K(18-crown-6)]$^+$ and [K]$^+$) and, thus, kinetics contribution. The formation of [**3**–A]$^-$ led to downfield shifts of δ^{125}Te by ~20 ppm in ^{125}Te NMR spectra, except [**3**–F]$^-$.[34(d)] For the latter, where the signal authenticity was unambiguously proved by the observation of the ^{1}J(^{19}F–^{125}Te/^{125}Te–^{19}F) in ^{19}F and ^{125}Te NMR spectra, the shift of δ^{125}Te was upfield.[34(b)] Solid-state ^{125}Te NMR independently confirmed the Te–N, not Te–O, *ChB* in [**3**–NCO]$^-$; for ^{125}Te NMR chemical shift tensors of [**3**–A]$^-$ (A = ECN; E = O, S, Se), however, no simple correlations with *ChB* distance or angle were found, which can be caused by long-range packing-effect contributions to the tensors.[50(f)]

The *K* constants of [M–A]$^-$ (A = Cl, Br) measured by VIS titration for M = **12** are significantly lower than for M = **2**, **3** indicating relatively weak *ChB* in [**12**–A]$^-$ in agreement with the corresponding Δ*G* magnitudes calculated by dispersion-corrected DFT. The QTAIM and NBO suggest that the *ChB* in [**12**–A]$^-$ is mainly electrostatic and dispersive in nature but with noticeable orbital contribution in the form of negative hyperconjugation.[73(a)]

Amongst [M–A]$^{2-}$ [A = **7**$_2$,[73(c)] Te$_n$ (*n* = 2, 4),[34(e)] SO$_4$[61(b)]], trimeric [**7**–**7**$_2$]$^{2-}$ is the most uncommon in the stereoelectronic aspect. It was obtained as unexpected product of reduction of **7** into [**7**]$^{\bullet-}$ radical anion (RA). The diamagnetic [**7**–**7**$_2$]$^{2-}$ is composed of antiferromagnetically-coupled diradical dianion ([**7**]$^{\bullet-}$)$_2$ in the singlet ground state and neutral molecule **7** bridged by unusually asymmetric Te–N *ChBs* (ESM). CASSCF suggests that the negative charge of [**7**–**7**$_2$]$^{2-}$ is delocalized over the whole specie; ~85% of the charge, however, is concentrated on the ([**7**]$^{\bullet-}$)$_2$ unit.[73(c)] In [**7**–Te$_2$]$^{2-}$ (see Figure 2) and [**7**–Te$_4$–**7**]$^{2-}$, only one σ-hole of **7** is used for [Te$_n$]$^{2-}$ (*n* = 2, 4) coordination.[34(e)] For putative [M–SO$_4$]$^{2-}$ (M = **1**–**3**), double Te–O *ChB* is suggested with M = **3** resembling double E–O *ChB* proposed for [M–NO$_3$]$^-$ (M = **1**, **2**).[61(b)]

For [M–A]$^{n-}$ (M = **1**–**3**, **7**, **9**, **11**, **13**; A = F, Cl, Br, I, NO$_3$, SO$_4$; *n* = 1, 2), EDA suggests that the *ChBs* are essentially, but not totally, electrostatic and relatively strong. The EDA-NOCV confirms the *n*→σ* character of CT. The strength of *ChB* depends not only on $V_{\mathrm{S,max}}$ at the M hosts but also on $V_{\mathrm{S,min}}$ at the [A]$^{n-}$ guests; with M = **1**–**3**, the relative strengths of the *ChBs* are generally in the A order SO$_4$ > F > Cl > Br > NO$_3$.[59,61(b)] The EDA/SAPT treatment of *ChB* in putative [**6**$_2$–A]$^-$ and real [**6**$_4$–A]$^-$ (A = Cl, Br, I) also reveals dominance of electrostatic interactions in front of orbital and dispersion ones; the dispersion energy is slightly [A]$^-$-dependent and provides ~10% of the *ChB* energy. Generally for *ChB*-bonded complexes, EDD and NBO jointly confirm [A]$^-$-depending CT associated with an orbital contribution.[24(a),61(b)]

In [M–A]$^{n-}$, *ChB* bcp's feature very low electron densities ρ_{b} = ~0.01−0.05 (hereinafter, in a.u.) except [M–F]$^-$ with

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[§§§] Cyanated or fluorinated (aza)arenes coordinate [A]$^-$ by means of [A]$^-$···π interactions driven by π-holes; fused with 1,2,5-chalcogenadiazoles, they coordinate [A]$^-$ by virtue of *ChB* based on chalcogen σ-holes.

ρ_b = ~0.1. For [**3**–A]$^-$ (A = CN, OCN, SCN, SeCN), ρ_b = ~0.04–0.08 depending on both A and its orientation. The highest ρ_b value relates to [**3**–CN]$^-$ revealing also the highest CT in this series. The values of Laplacian $\nabla^2\rho_b$ at the bcp's are relatively small and positive. Such ρ_b and $\nabla^2\rho_b$ are typical of mainly electrostatic/closed-shell interactions. At the same time, the ratio of potential V_b and kinetic G_b energy densities, $1 < |V_b|/G_b < 2$, indicates their partially covalent character. The QTAIM/NCI situate the *ChB* in [M–A]$^{n-}$ in the same energy range as strong *HB*.[24(a),33(b),34(a),(b),(d),(e),59,61(b),73(a)]

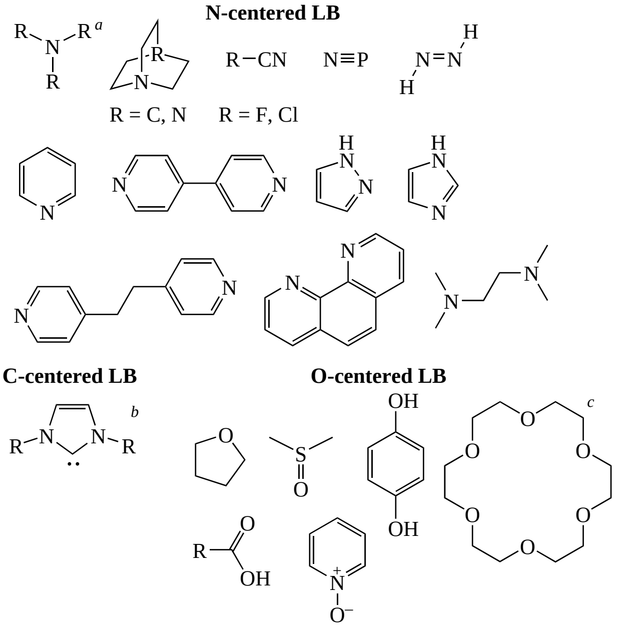
Quantum-chemically estimated thermodynamics suggests the general character of the [M–A]$^-$ formation for M = 1,2,5-selena/telluradiazoles, covering in some cases thiadiazoles. Numerically, *ChB* energy depends on the computational method and for M = **1**–**3** varies in a wide range from ~25 in putative [**1**–I]$^-$ to ~97 kcal mol^{-1} in putative [**3**–SO$_4$]$^{2-}$. The lower limit is comparable to the energy of weak covalent bonds, *e.g.* internal N–N bond in organic azides; and the upper limit, to that of the C–C bond in common organics.[33(a),(b),34(a)–(c),61(b)]

For [A]$^-$ receptor chemistry,[3(d),5(c)–(e),10(a),(b),78] very important is recognition selectivity in the situations where the guest deals with non-equivalent binding sites of the host; or the host deals with a set of guests. In the latter case, a wide disparity in the *ChB* strengths may lead to the selective complexation of specific [A]$^-$. Both situations are poorly studied. Thus, [Cl]$^-$ selects between S and Se binding sites of **4** (see Figure 1) forming [**4**–Cl]$^-$ with the Se–Cl *ChB* (see Figure 2). A preliminary assessment of selectivity of **3** towards [F]$^-$ and [SeCN]$^-$ with 1 : 1 : 1 mixture of **3**, [F]$^-$ and [SeCN]$^-$ revealed of the Te···F interactions with the formation of [**3**–F]$^-$ in accordance with thermodynamics.[34(d)] Competitive comparison of **3** with established [A]$^-$-receptor (*o*-C$_6$F$_4$Hg)$_3$ **15**[6] with the 1 : 1 : 1 mixture of **3**, **15** and [SeCN]$^-$ disclosed dominance of **15** with the formation of [**15**–SeCN]$^-$.[34(d)] Individual **15** coordinates chalcogenadiazoles *via* Hg···N and F···H SBIs.[79]

Limitations of [A]$^-$ recognition with 1,2,5-chalcogenadiazoles are associated with (1) unfavorable thermodynamics, for which easily-available $V_{S,max}$ of hosts can be used as *a priori* indicators; and (2) guests-induced decomposition of the hosts or their reduction into RAs. The first limitation refers to sulfur/selenadiazoles; particularly, [M–A]$^{n-}$ (M = **1**, **2**, A = any tried anion; M = **5**, **8**, **10**, A = halide) are not observed.[24(a),34(d),73(b),80] The second limitation concerns telluradiazoles. Thus, the reactions of **3** with [PhTe]$^-$,[34(b)] **7** with [A]$^-$ [A = F, RO (R = Ac, Tf), HSO$_4$, H$_2$PO$_4$] (in contrast with A = Cl, Br, I, NO$_3$),[34(c)] and **1**, **2** and their fused derivatives with charged C-nucleophiles (crypto-anions of organometallics, metal = Li, Mg),[77] lead to the hosts disintegrations. On a practical level, work with telluradiazoles is also complicated by their hydrolytic instability. In the form of chemical reduction, this limitation covers hosts with enhanced electron affinity (EA)[¶¶¶,24(c),37] and guests enabling act as reducing agents. Thus, **2**–**4** and all-S congener of **4** with [PhE]$^-$ (E = S, Se), and **12** with [CO$_3$]$^{2-}$, afford corresponding RAs.[19(a),33(a),34(a),43(d),81]

Neutral molecules

Towards real or putative M–LB (M = **1**–**13**), N-, C- and O-centered LBs are studied (Scheme 2). For N-centered ones, all *sp*^{n} hybridization states (n = 1–3) are covered; heavier pnictogens are represented by Me$_3$As. The O-centered LBs encompass phenols, particularly, 4-NO$_2$ derivative. The isolated complexes are characterized by XRD (Figure 4; ESM) (for **2**–PNO polymorphism is found), solid-state NMR, and quantum chemical calculations. As in [M–A]$^{n-}$, in M–LB guests function as mono- or ditopic ligands, and *ChB* is longer than the sum of the covalent radii of the partner atoms but shorter than the sum of their VdW radii. In many cases, significant cooperativity of *ChB* and other SBIs is observed.[19(b),25(b),(c),26(e),33(b),34(a),50(a)–(d),59,75,82,83]



Scheme 2 N-, C, and O-centered LBs studied with chalcogenadiazoles **1**–**13**; ^{a}covers heavier-pnictogen analogue Me$_3$As; ^{b}N-heterocyclic carbenes; ^{c}covers dibenzo-18-crown-6.

The M–LB (M = **2**, **3**; LB = BP, BPE, DAP)[50(c)] and Py–**3**–Py[33(b)] feature double *ChB*; and **11**–Py,[25(c)] supramolecular dimers. The overall CT of ~0.1 in Py–**3**–Py is expectedly much lower than ~0.3 in [**3**–Cl]$^-$ and [Cl–**3**–Cl]$^{2-}$.[33(b)] For **7**–Q of M–Q family (M = **7**, **9** and its 4-CN isomer, **11**, **13**),[34(c),59,75] K weakly depends on the nature of solvents[34(c)] (ESM). According to quantum chemical calculations at various levels of theory, putative M–LB$_n$ [M = **10**, **11** and their S-congener **16**; LB = Py, Pyr, Im, R–CN (R = F, Cl), N≡P, *trans*-N$_2$H$_2$; n = 1, 2] are realistic with *ChBs* having predominantly electrostatic character; in going from **16** to **11** and **10**, the electrostatic and polarization contributions gradually increase and the dispersion contribution decreases. The ρ_b, $\nabla^2\rho_b$ and CT values for M–LB$_n$ are noticeably lower than for [M–A]$^{n-}$. With LB = Py, Im, *ChB* is stronger than *HB*. On the addition of a second LB to M–LB, *ChB* gets weakened.[82(a)] Complexes of **3** with DABCO[50(e)] and TMEDA[83] are 1D coordination polymers; with TMEDA, they have [**3**·M]$_\infty$ and [**3**$_2$·**M**]$_\infty$ structures, and also form [**3**$_2$·M]·Solv clathrates (M = TMEDA; Solv = benzene, pyridine, or thiophene).[83] From a vapor phase, environmentally-hazardous heavier-pnictogen compound Me$_3$As forms complexes with some derivatives of **5**, which, consequently, is a promising platform for effective FL sensors of Me$_3$As vapor possessing rapid response, together with high sensitivity and selectivity; the S congeners are less effective.[82(b)]

For real (M = **3**, **7**; see Figure 4)[50(a)] and putative (M = **13**)[59] M–NHC, quantum chemical calculations suggest the major electrostatic contribution in the *ChB* (ρ_b of ~0.04–0.06 and small positive $\nabla^2\rho_b$) in front of non-negligible orbital contribution. The latter is based on the donation of a NHC's unshared electron pair to the Te atom. For M = **3**, **7**, the Roby[84(a)] and Raub–Jansen[84(b)] bond indices indicate a highly polarized but strongly covalent character of this interaction.[50(a),59] The *ChB* polarization is characterized by CT of ~0.1–0.3 from Mulliken, NBO, Hirshfeld, and QTAIM analyses; as with [A]$^-$, the higher values come from

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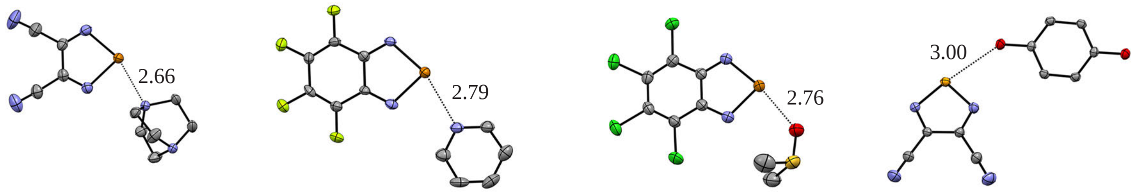
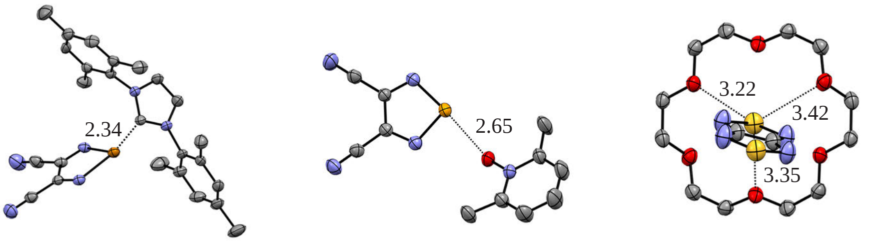
[¶¶¶] Most of 1,2,5-chalcogenadiazole derivatives are strong π-acceptors. Their first adiabatic EA is positive, which means that π-RAs are thermodynamically more preferable than the neutral molecules.



3–DAB[50(c)] CCDC 1940765 **11**–Py[25(c)] CCDC 821132 Cl$_4$–**7**–DMSO[24(c)] CCDC 2165318 **2**–HQ[50(d)] CCDC 2174994



3–NHC[50(a)] CCDC 1526517 **2**–PNO[47(c)] CCDC 2016657 all-S **4**–CR[19(b)] CCDC 1995137

Figure 4 Representative XRD structures of neutral complexes (ESM); H atoms are omitted for clarity. The *ChBs* are indicated by dashed lines with bonds distances in Å. Colour code: C – grey, Cl – green, F – lemon green, N – blue, O – red, S – yellow, Se – golden yellow, Te – orange.

Mulliken scheme. The calculated *ChB* order is ~0.5. For M = **3**, **7**, such a low value is qualitatively proved by variable-temperature NMR in THF solutions revealing free rotation of molecular fragments around *ChB*, together with inversion; the NHC-depending energy barrier of the inversion estimated with Eyring equation is $\Delta H^{\neq}$ of ~10 kcal mol^{-1} and $-\Delta S^{\neq}$ of ~6 ± 4 cal mol^{-1} K^{-1}.[50(a)]

Amongst M–LB (M = Cl$_4$–**7**, **13**, LB = DMSO; and M = **13**, LB = THF),[24(c),25(b),34(c),59] those with LB = DMSO feature supramolecular dimers in the solid state. Complex **5**–(4-O$_2$NC$_6$H$_4$OH) reveals cooperativity of *ChB* (Se–N and Se–O), *HB* (N–H) and **5**···**5** π-stacking interactions.[82(d)] The *ChB* nature of M–HQ (M = **2**, **3**) is confirmed by XRD (see Figure 4) and solid-state NMR;[50(d)] and M–CR (M = **2**, **3** and all S-analogue of **4**), by XRD (see Figure 4), DFT, QTAIM and NBO.[19(b)] Quantum chemical calculations and QTAIM analysis of M–CR suggest predominantly electrostatic character of the E–O *ChB*; the corresponding ρ_b, $\nabla^2\rho_b$ and CT values are noticeably lower than for $[M–A]^{n-}$.[19(b)] The E–O *ChB* (E = Se, Te) of M–PNO (M = **2**, **3**) (see Figure 4) exists in both solid state (XRD, see Figure 4; solid-state NMR) and organic solutions (solution NMR).[50(b),(c)] Similar E–O *ChB* between PNO-based surfactant and quasi-calix[4][1,2,5-chalcogenadiazole] drives solution self-assembly of supramolecular nanofibers (E = Se) or vesicles (E = Te) with supra-amphiphilic properties. The *ChB*-competing $[A]^-$ (A = Cl, Br) or decreased pH provoke reversible disassembly.[82(c)]

In indirect way, the title compounds were also used in recognition of neutral molecules which are not LBs. The crystal structures of 1,2,5-chalcogenadiazoles, their 2-oxides and 1,2,5-chalcogenadiazolium salts are self-assembled by $[E–N]_n$ (n = 1, 2) *ChBs*.[23(a),24(a)–(c),25(b)–(f),26(a)–(h),27,28,38,41(b),63] Some structures have VdW voids capable of filling; in triptycene tris(1,2,5-selenadiazole), incremental single-atom substitutions of Se with Te promotes assembly of stable low-density *ChB*-based frameworks.[27] For CN-containing, especially TCNQ-fused, derivatives the voids formed by E–N$_{CN}$ (E = S, Se) *ChBs*, spatially match some arenes.[17(f),85] With E = Se, the voids of these strongly π-accepting compounds[¶¶¶,24(c),37] are effective in selective molecular recognition/separation, *e.g.* of isomeric methylated benzenes or naphthalenes, by means of the CT-type clathrate formation.[17(f),85(b)] Similar situation is observed for cavitands based on resorcin[4]arene and **5**, **7** or their S congener and self-assembled into supramolecular capsules by the $[E–N]_2$ *ChBs*. The cavities' volumes depend on E–N distances (stronger is the *ChB*, shorter is the distance), and the Te derivative with smaller cavities is capable of forming clathrate with benzene; whereas the S analogue with bigger cavities, with toluene.[29(a)] The *ChB*-bonded supramolecular containers formed by selenadiazolo-based cavitand selectively encapsulate (functional) alkanes; both unloaded and loaded containers reveal enhanced magnetic anisotropy.[86]

Limitations of recognition of neutral LBs by 1,2,5-chalcogenadiazoles relate to addition reactions of hosts possessing higher EA (*e.g.* azabenzo-fused derivatives)[37] with C-nucleophilic/CH-acidic guests.[38,87]

Conclusion

The title compounds are promising for *ChB*-based chemical recognition/sensing of Lewis bases. Their known structural variations are really countless, and **1–13** represent only a very limited set. The cyclic/heteroaromatic structure of 1,2,5-chalcogenadiazole is important for the subject since (R–N=)$_2$E acyclics are not effective in the field. The *ChB* of the title compounds exhibits clear-cut covalency highlighting the misleadingness of the term noncovalent interactions in this context.[†] In the form of CR-annulated derivatives,[81(b),88] the title compounds have the unexplored potential for cooperative ion-pair recognition. Further research should focus on enhancing selectivity, sensitivity, and applicability, aligning with the criteria expected for an ideal chemosensor, with fluorescence detection being particularly suitable. For practical applications, recognition/sensing in water and air are essentially important, *e.g.* for the detection of environmental contaminates. In this regard, water-stable Se derivatives are the most encouraging; whereas the S congeners are weaker *ChB* donors, and Te ones are moisture sensitive. On the other hand, under water-free conditions low-soluble Se and Te derivatives can be used as solid-state sensors performing at the solid–liquid and solid–gas interfaces. Consequently, hydrophilic 1,2,5-selenadiazoles have to be designed, synthesized, and characterized, including their hybrids with 1,3-di- or/and 1,2,3-triazoles allowing *ChB* and *HB* cooperativity. For the design purposes, easily-available $V_{S,max}$ can be used. Based on available data, $V_{S,max}$ threshold of ~30 kcal mol^{-1} might be taken for the hosts of small $[A]^{n-}$. At the same time, EA of the hosts should be lower ~1 eV[24(c),37,73(b)] to prevent reduction into RAs with $[A]^-$ guests, as well as addition of neutral C-nucleophilic/CH-acidic guests.

In the fundamental aspects, interaction of the title compounds with $[F]^-$ (*cf.* $[$**3**$–F]^-$)[34(b)] is useful for experimental quantitative assessment of Lewis acidity of main-group compounds *via* fluoride-ion affinity (FIA).[††††,89] Another interesting possibility is *ChB* sterical switching between σ- and π-holes.[64] On $V_{\mathrm{S,max}}$ scale, π-holes are generally weaker than σ-holes but have advantage in better overlap of MOs responsible for *ChB* covalency and CT.[56] This may lead to stronger VIS/FL response facilitating detection. Besides, interaction of the title compounds with $[A]^{n-}$ affords new chemical bonds including challenging, *e.g*. those between different E atoms. This interaction can be expanded onto trapping exotic $[A]^{-}$[‡‡‡‡,90] RAs and other transient species, *e.g*. reaction intermediates including those of catalytic processes in solution, *etc*.

Overall, the discussed findings highlight once again the special significance of chalcogen-nitrogen π-heterocyclic chemistry covering not only molecular/ion recognition and sensing but also many other hot topics, particularly molecular conductors and magnetics.[19(a),81,91]

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2024.04.001.

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