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

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Figure S1 represents selected XRD structures of anionic complexes $[M–A]^{n–}$, and Figure S2 those of neutral complexes M–LB; M = 1,2,5-chalcogenadiazole, chalcogen = S, Se, Te; $A^{n–}$ = anion; and LB = neutral Lewis base.

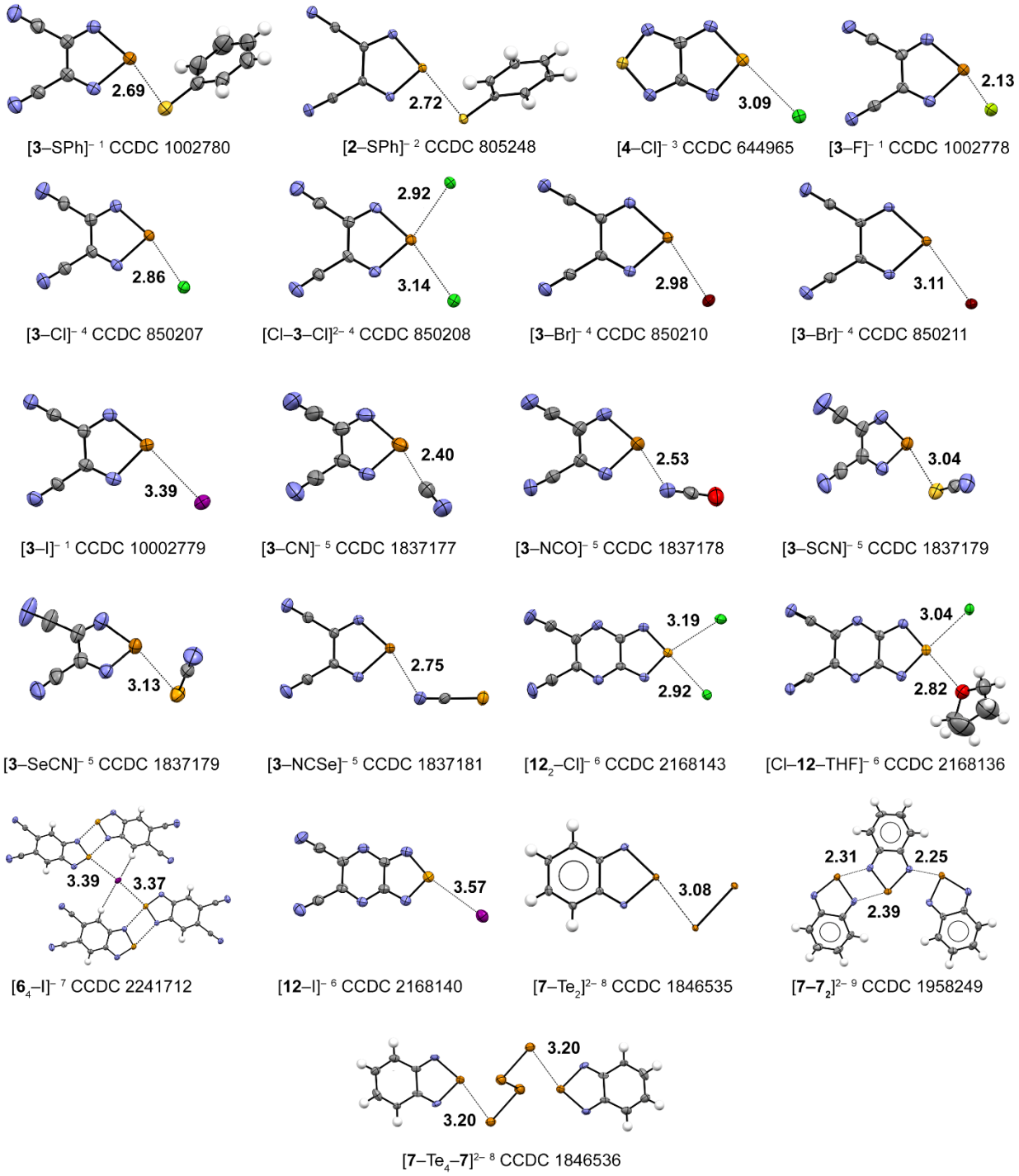


Figure S1 Selected XRD structures of complexes between 1,2,5-chalcogenadiazoles and anions. The *ChBs* are indicated by dashed lines with bonds distances in Å. Colour code: C – grey, H – light gray, Br – dark red, Cl – green, F – lemon green, I – purple, N – blue, O – red, S –yellow, Se – golden yellow, Te – orange. Omitted $[Cat]^+$: $[K(18\text{-crown-6})]^+$ for $[\mathbf{2}–SPh]^-$, $[PhS–\mathbf{3}–THF]^-$, $[\mathbf{3}–A]^-$(A = I, CN, NCO, SCN, SeCN), $[\mathbf{7}–Te_2]^{2-}$, $[\mathbf{7}–Te_4–\mathbf{7}]^{2-}$, $[\mathbf{7}–\mathbf{7}_2]^{2-}$, $[\mathbf{12}–I]^-$; $[PyH]^+$ for $[\mathbf{3}–A]^-$ (A = Cl, Br), $[Cl–\mathbf{3}–Cl]^{2-}$, $[\mathbf{4}–Cl]^-$; $[Et_4N]^+$ for $[\mathbf{6}_4–I]^-$, $[Cl–\mathbf{12}–THF]^-$, $[\mathbf{12}–Cl–\mathbf{12}]^-$; $[(Me_2N)_3S]^+$ for $[\mathbf{3}–F]^-$; $[K]^+$ for $[\mathbf{3}–NCSe]^-$.

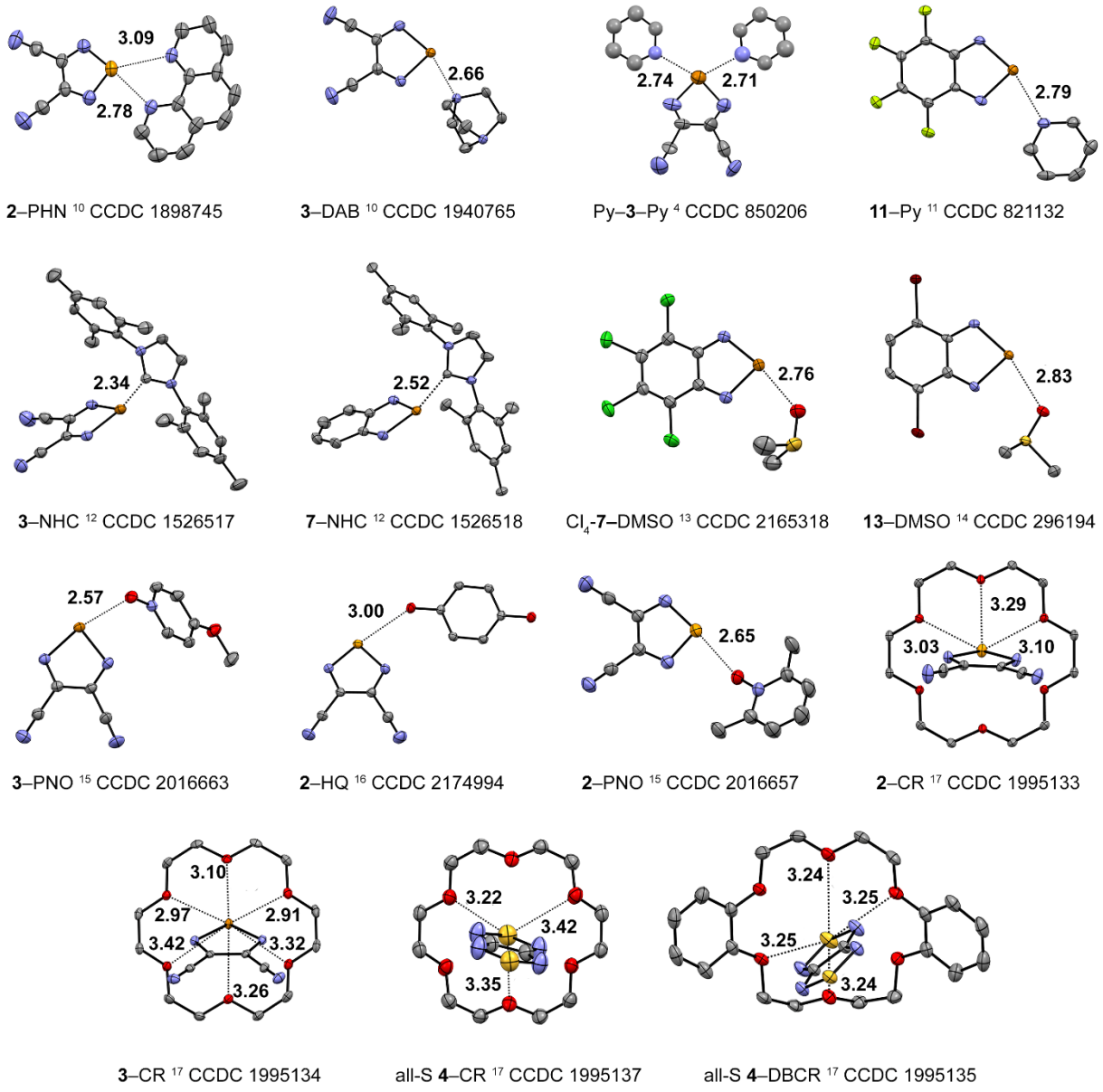


Figure S2 Selected XRD structures of complexes between 1,2,5-chalcogenadiazoles and neutral molecules; H atoms are omitted for clarity. The *ChBs* are indicated by dashed lines with bonds distances in Å. Colour code: C – grey, N – blue, O – red, S – yellow, Se – golden yellow, Te – orange.

Stability of complexes

Tables S1 and S2 contain experimental and theoretical data on stability of anionic complexes [M–A]$^{n-}$ and neutral complexes M–LB; M = 1,2,5-chalcogenadiazole, chalcogen = S, Se, Te; A^{n-} = anion; and LB = neutral Lewis base.

Table S1 Experimental association constants K and experimental and DFT-calculated Gibbs free energy ΔG of anionic complexes[a,S1,S5,S18]

Complex	$K\times10^3$, M^{-1} ($-\Delta G$, exp. / DFT;[b] kcal mol^{-1})	
	THF	MeCN
	1	
[**1**–CN]$^-$	– (– / –2.5)	– (– / –6.9)
[**1**–NC]$^-$	– (– / –3.5)	– (– / –6.4)
[**1**–OCN]$^-$	– (– / 0.0)	– (– / –4.1)
[**1**–NCO]$^-$	– (– / 0.8)	– (– / –2.8)
[**1**–SCN]$^-$	– (– / 0.2)	– (– / –3.2)
[**1**–NCS]$^-$	– (– / –0.2)	– (– / –2.6)
[**1**–SeCN]$^-$	– (– / 0.0)	– (– / –2.7)
[**1**–NCSe]$^-$	–	– (– / –1.4)
[**1**–TeCN]$^-$	– (– / –1.3)	– (– / –3.7)
[**1**–NCTe]$^-$	– (– / –1.7)	– (– / –4.0)
	2	
[**2**–CN]$^-$	– (– / 4.1)	– (– / –1.6)
[**2**–NC]$^-$	– (– / 1.8)	– (– / –2.3)
[**2**–OCN]$^-$	– (– / 2.6)	– (– / –1.3)
[**2**–NCO]$^-$	– (– / 5.7)	– (– / 0.9)
[**2**–SCN]$^-$	– (– / 4.5)	– (– / –0.5)
[**2**–NCS]$^-$	– (– / 2.4)	– (– / –1.4)
[**2**–SeCN]$^-$	– (– / 4.0)	– (– / 0.2)
[**2**–NCSe]$^-$	–	– (– / –1.4)
[**2**–TeCN]$^-$	– (– / 2.5)	– (– / –0.9)
[**2**–NCTe]$^-$	– (– / 0.4)	– (– / –3.3)
	3	
[**3**–F]$^-$	– (– / 33.1)	
[**3**–Cl]$^-$	– (– / 16.7)	
[**3**–Br]$^-$	– (– / 12.8)	
[**3**–I]$^-$	680[c] (– /– 5.7)	1.5
[**3**–CN]$^-$	– (– / 12.7)	– (– / 6.4)
[**3**–NC]$^-$	– (– / 7.6)	– (– / 2.5)
[**3**–OCN]$^-$	– (– / 6.4)	– (– / 1.2)
[**3**–NCO]$^-$	– (– / 10.6)	– (– / 6.9)
[**3**–SCN]$^-$	– (– / 13.5)	0.50 (3.7 / 5.0)
[**3**–NCS]$^-$	– (– / 8.3)	– (– / 2.9)
[**3**–SeCN]$^-$	– (– / 10.3)	0.70 (3.8 / 5.1)
[**3**–NCSe]$^-$	– (– / 7.1)	– (– / 2.2)
[**3**–TeCN]$^-$	– (– / 9.3)	– (– / 3.6)
[**3**–NCTe]$^-$	– (– / 4.1)	– (– / –0.4)

[**3**–SPh]$^-$	74	3.0
	7	
[**7**–Cl]$^-$	0.97 (4.1 / 3.5)	0.07
[**7**–Br]$^-$	0.19 (3.1 / 1.2)	0.03
[**7**–I]$^-$	–	0.01
[**7**–NO_3]$^-$	0.02 (1.6 / 0.7)	–
	9	
[**9**–Cl]$^-$	38 (6.2 / 6.7)	–
[**9**–Br]$^-$	2.2 (4.6 / 3.7)	–
[**9**–NO_3]$^-$	0.08 (2.6 / 2.1)	–
	11	
[**11**–Cl]$^-$	130 (7.0 / 7.5)	–
[**11**–Br]$^-$	9.8 (5.4 / 4.6)	–
[**11**–NO_3]$^-$	0.19 (3.1 / 2.7)	–
	13	
[**13**–Cl]$^-$	12.2 (5.6 / 6.5)	–
[**13**–Br]$^-$	1.2 (4.2 / 4.5)	–
[**13**–NO_3]$^-$	0.08 (2.6 / 0.2)	–

[a] The $[A]^-$ = $[F]^-$, $[HSO_4]^-$, $[H_2PO_4]^-$, $[AcO]^-$ and $[TfO]^-$ decompose benzotelluradiazoles **7**, **9**, **11**, and **13**.[S18] [b] B97-D3/def2-tzvp for $[A]^-$ = $[Cl]^-$, $[Br]^-$, $[I]^-$, $[NO_3]^-$, and $[PhS]^-$ with the PCM solvent model for THF;[S18] and for $[A]^-$ = $[CN]^-$and $[ECN]^-$ (E = O, S, Se, Te) with the COSMO model for THF and MeCN.[S5] [c] In CH_2Cl_2.

Table S2 Experimental association constants *K* and experimental and DFT-calculated Gibbs free energy *ΔG* of neutral complexes with quinuclidine[a] (Q) in THF[S18]

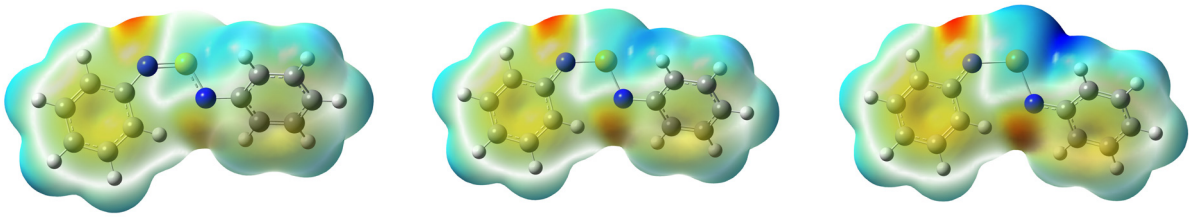
Complex	~$K\times10^3$, M^{-1} (–ΔG, exp. / DFT;[b] kcal mol^{-1})
6–Q	0.02[c] (1.7 / 0.9)
8–Q	0.05 (2.4 / 2.7)
10–Q	0.10 (2.7 / 3.6)
12–Q	0.06 (2.4 / 2.2)

[a] 1-Azabicyclo[2.2.2]octane. [b] B97-D3/def2-tzvp with the PCM solvent model for THF. [c] 0.04 in MeCN.

Acyclic analogues

Similar to 1,2,5-chalcogenadiazoles, their (R–N=)$_2$E (E = S, Se, Te) acyclic analogues analyzed here in dominant *Z,E* configurations[S19-S21] feature MEP holes. However, the $V_{S,max}$ magnitudes at chalcogen atoms (Figure S3) are markedly lower than for related heterocycles (*cf.* 24 kcal mol^{-1} for putative (Ph–N=)$_2$Te with 28.0 kcal mol^{-1} for **7**; for real (Ph–N=)$_2$S the σ-hole at the S atom is

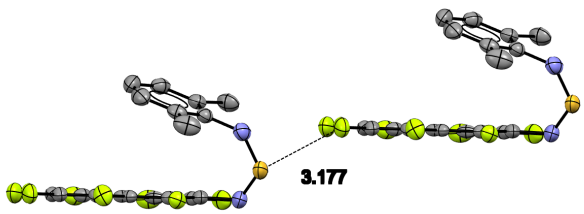
very weak). Notably, σ-holes in the *Z,E* configurations are shared between the chalcogen and *ortho*-H atoms of the *E*-Ph, which could facilitate SBIs, *i.e.*, simultaneous *ChB* and *HB* formation. Overall, without carbocyclic substitution by electron-acceptor groups the discussed acyclics are expected to be weak LB receptors. Indeed, reported reactions between $(R–N=)_2S$ and $[A]^-$ proceed as π-addition (*i.e.*, primary bonding interaction) of $[A]^-$ to the considerably polarized double bonds;[S20,S23,S24] the addition of crypto C-anions of organolithium and -magnesium compounds to $(R–N=)_2S$ is even recommended as a simple method of quantitative determination of these organometallics.[S24] Complexes / solvates with neutral LBs are unknown.



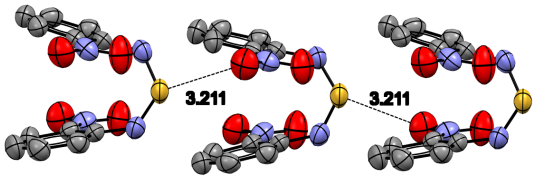
E = S, 16.6 E = Se, 19.0 E = Te, 24.4

Figure S3 B3LYP/def2-tzvp-calculated MEPs (0.001 e $Bohr^{-3}$ isosurfaces) of real (E = S) / putative (E = Se, Te) *Z,E*-$(Ph–N=)_2E$ optimized at the same level of theory, together with $V_{S,max}$ (kcal mol^{-1}) of σ-holes. MEP colour code: blue – positive, red – negative; atom colour code: C – grey, H – light grey, N – blue, S – yellow.

At the same time, solid-state structures of four individual $(Ar–N=)_2S$[S25-S28] featuring shortened S…X intermolecular contacts are published; notably, one compound is in the *Z,E* configuration, whereas three other are in the *Z,Z* (Figure S4). It is unclear, whether these contacts are *ChBs*. In any way, potential of $(R–N=)_2E$ in the context of *ChB* is worth a closer look. Particularly for E = S, $Ar–E_k–(N=E=N–E–)_l–N=E=N–S_m–Ar$ (k, m = 0, 1; l = 0, 1) structurally-flexible catenated compounds are known;[S19,S20,S29] the most extended (k = l = m = 1) represent σ-hole garlands.



CCDC 154394 [S25]



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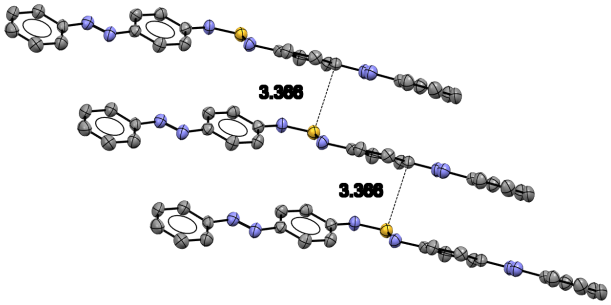

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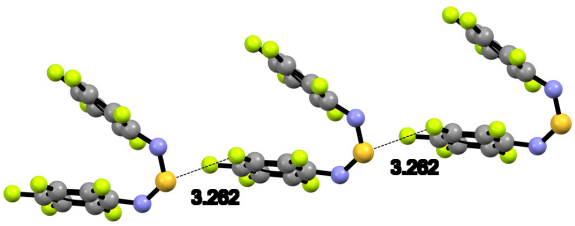

CCDC 1237174 [S28]

Figure S4 Fragments of XRD structures of $(Ar–N=)_2S$ featuring shortened S…X intermolecular contacts; H atoms omitted. Colour code: C – grey, F – light green, N – blue, O – red, S – yellow.

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