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Charge-transfer chemistry of chalcogen–nitrogen π-heterocycles

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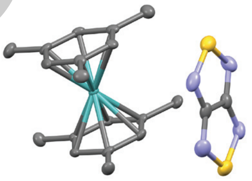
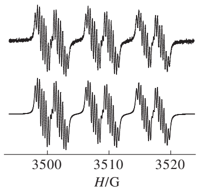
Recent achievements in the charge-transfer chemistry of 1,2,5-chalcogenadiazoles, 1,2,3-dichalcogenazoles (chalcogen is S, Se, or Te), their fused congeners and hybrids are discussed with special emphasis on the synthesis and structural and functional characterization of radical anions, radical-anion salts, charge-transfer complexes, neutral and charged donor–acceptor complexes, and metal coordination compounds.





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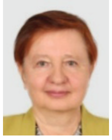

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Introduction

Unsaturated chalcogen–nitrogen derivatives (chalcogen = S, Se, or Te),[†] both acyclic and cyclic, reveal different properties interesting for chemistry and materials science, which are not observed in any other compounds.[1] In materials science, they are best known with molecular metal and superconductor $(SN)_x$[2] and molecular conductors and magnets based on 1,2,3-dithiazolyls (Herz radicals) and 1,2,3,5-dithiadiazolyls, their Se congeners, and other thiazyl radicals.[3] Whereas $(SN)_x$ is of only theoretical significance, the radicals, which are stable in a solid state, can find applications in organic electronics and/or spintronics.

Here, we consider chalcogen–nitrogen π-heterocycles,[4] from which 1,2,5-chalcogenadiazoles, 1,2,3-dichalcogenazoles, and their fused derivatives and hybrids (Figure 1) were selected for discussion due to their importance for fundamental and applied chemistry and functional materials science.[‡,1,3,5] 1,2,5-Chalcogenadiazoles are closed-shell neutral S, Se, and Te compounds, whereas 1,2,3-dichalcogenazoles are best known as the Appel and Herz cations and the Herz radicals (Figure 1).[3,6,7] To transform them into closed-shell neutral species, structural modification is necessary (Figure 1; R = O, $C(CN)_2$, or a fused cycle fragment).[4(*d*),8] The chemistry of Se-containing congeners is in its infancy, whereas Te-containing species are undescribed.[4(*d*)]

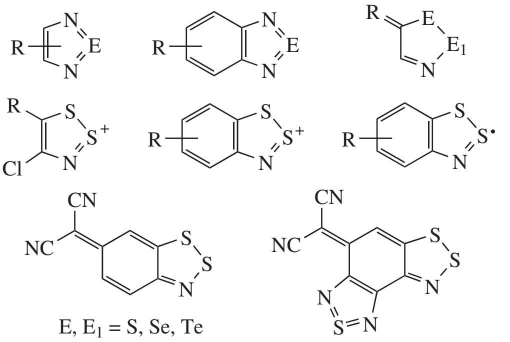

Figure 1 1,2,5-Chalcogenadiazoles, 1,2,3-dichalcogenazoles, their hybrid, 1,2,3-dithiazoliums (Appel and Herz cations) and 1,2,3-benzodithiazolyls (Herz radicals).

Here we consider recent achievements in the charge-transfer (CT) chemistry of selected heterocycles with special attention to the synthesis and structural and functional characterization of new radical anions (RAs), RA salts, CT and donor–acceptor (DA) complexes,[§,9] and metal coordination compounds. Methods for the syntheses of heterocycles are not specified since they are well-established in most cases.[4(*a*),10] However, recently suggested approaches should be highlighted,[11(*b*),12,13] first of all, those based on selective chalcogen exchange.[4(*d*),13,14(*d*)]

Positive electron affinity

Despite 2,1,3-benzothia(selena)diazoles were successfully used as electron acceptors for a long time,[4(*a*),14] the physical background of this was discussed in the explicit way only recently.[4(*a*),15] With DFT calculations on 1,2,5-chalcogenadiazoles, 1,2,3-dichalcogenazoles, their hybrids and other chalcogen–nitrogen π-heterocycles, it was shown that the first adiabatic electron affinity (EA_1) of the compounds is positive (Figure 2). For the heterocycles, it means that their RAs are thermodynamically more preferable than the neutral molecules.[4(*a*),15] Importantly, with DFT calculations and cyclic voltammetry, it was found that EA_1 increases with the atomic number of the chalcogen in the isostructural series of chalcogenadiazoles (see Figure 2).[4(*a*),4(*g*),11] This trend is nontrivial since it contradicts the atomic EA (S, 2.08 eV; Se, 2.02 eV; Te, 1.97 eV) and electronegativity (Allen scale: S, 2.59 eV; Se, 2.42 eV; Te, 2.16 eV) of chalcogens. It can be tentatively explained by a better charge/spin delocalization in the diffuse π*-SOMOs of RAs containing heavier chalcogens. Substitution in a carbocycle, where possible, with electron withdrawing groups also increases the EA_1 (see Figure 2). Both trends can be used in the design and synthesis of compounds with increased positive EA_1.

Because of positive EA_1, many chalcogen–nitrogen π-heterocycles serve as efficient electron acceptors in various CT processes

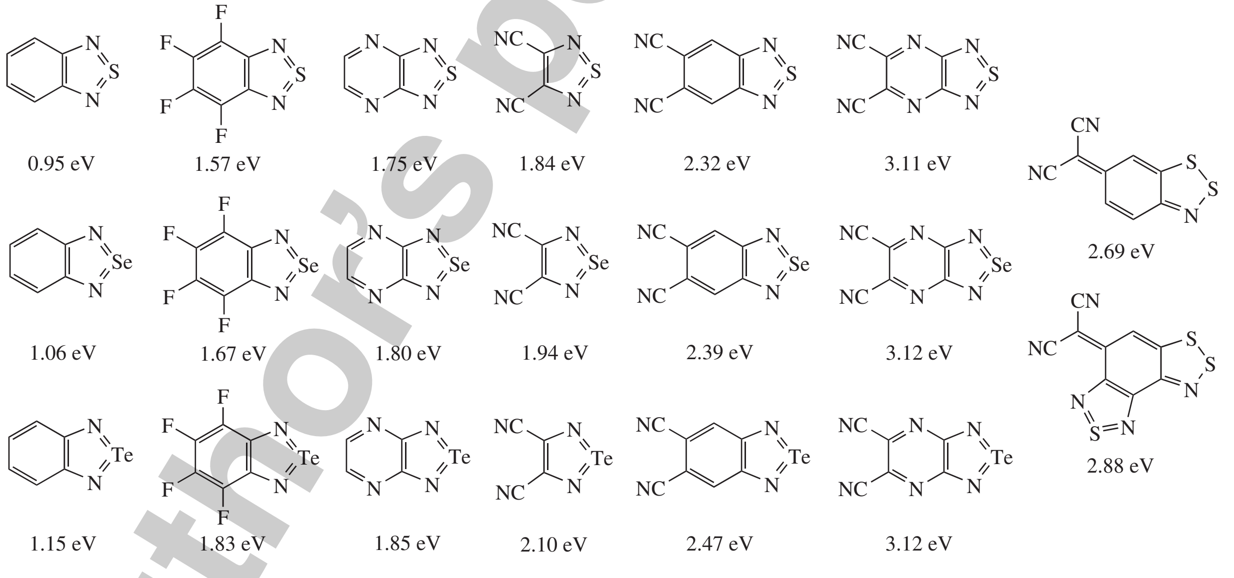

Figure 2 (U)B3LYP/6-31+G(d)-calculated EA_1 of chalcogen–nitrogen π-heterocycles (tetracyanoethylene, 3.48 eV).

[†] The chalcogens (Group 16) include O, S, Se, Te, and Po. However, O is frequently excluded from the scope of the term since the properties of its derivatives are normally different from those of other members of Group 16. Polonium–nitrogen π-heterocycles are unknown but their existence is not forbidden and DFT-calculated properties of 1,2,5-polonadiazoles match up the general picture: A. M. Genaev and A. V. Zibarev, unpublished results.

[‡] Both heterocyclic systems can find actual or potential applications. For closed-shell derivatives, those cover electroluminescence, photovoltaics, solar cells, chemical sensors, and fluorescent thermometers for living systems. Open-shell compounds are of interest as spin and/or charge carriers for organic electronic and spintronic devices.

[§] Boundaries between CT and DA complexes are vague. Here, these terms are used in their traditional meaning: the CT complex is a DA complex characterized by electronic transitions to an excited state, in which there is a partial transfer of electronic charge from a donor to an acceptor.

with electron donors, thus revealing the properties of Lewis acids. Note that CT between an electron donor and an acceptor can be full or partial. The full CT leads to acceptor RAs, whereas the partial CT leads to CT and DA complexes.[§,9]

Lewis ambiphilicity

Importantly, 1,2,5-chalcogenadiazoles are not only electron acceptors, *i.e.* Lewis acids, but also electron donors, *i.e.* Lewis bases, which is a rare case. The Lewis ambiphilicity of these heterocycles is primarily manifested in their propensity to self-association *via* E···N secondary bonding interactions ($[E\cdots N]_2$ supramolecular synthons; E = S, Se, Te) in a solid state, solution, and even gas phase. The interactions, in which E is an acceptor center and N is a donor one, increase in the order S, Se, and Te.[16] Another manifestation of the Lewis ambiphilicity of these heterocycles is their ability to coordinate metal cations[17] and a Lewis acid such as trimeric perfluoro-*ortho*-phenylenemercury[18,19] by N atoms and to form CT complexes, where both the electron donor and acceptor are 1,2,5-chalcogenadiazoles.[4(e),14(c)] This Lewis ambiphilicity can be used in the supramolecular chemistry and crystal engineering,[10(d),16] design and synthesis of functional materials,[4(e),14(c),17] and, potentially, in frustrated Lewis pair catalysis[20] with a single compound instead of a pair.

Radical anions

The RAs of the heterocycles under discussion were electrochemically and chemically generated in solution with various reducing agents in the latter case. 1,2,5-Thia(selena)diazolidyls (including polyfluorinated benzo-fused derivatives) and hybrid 1,2,5-thiadiazolidyls/1,2,3-dithiazolidyls revealed stability, and electrochemical reduction was reversible in most cases.[4,11,21,22] The RAs, however, were unstable towards air. Heterogeneous contact of a 1,2,5-thiadiazolidyl salt with moist air disclosed unusual reaction (Figure 3).[23] For 2,1,3-benzothia(selena)diazolidyls, decomposition in solution into corresponding $[ECN]^-$ (E = S or Se) upon contact with air was found, whereas for 2,1,3-benzotelluradiazolidyl 1 : 1 DA complex between its parent heterocycle and $[Te_2]^{2-}$ was observed together with further transformation into 2 : 1 complex between the telluradiazole and $[Te_4]^{2-}$.[4(g)]

1,2,5-Thia(selena)diazolidyls, their benzo- and azabenzo-fused derivatives and hybrid 1,2,5-thiadiazolidyls/1,2,3-dithiazolidyls from electrochemical and chemical reduction were characterized by EPR spectroscopy in combination with DFT calculations.[5(b),11,15,21,22] According to DFT, in the isostructural series the RAs are isolobal and possess π*-SOMOs causing elongation of the E–N (E = S, Se, and Te) bonds on going from neutral precursors to RAs.[4(a),4(g)] For 2,1,3-benzochalcogenadiazoles, the S-, Se-, and Te-containing RAs were detected. The EPR spectra revealed line broadening and *g* shift with the atomic number of the chalcogen[4(g)] caused by stronger spin–orbit coupling (SOC) in heavier chalcogens.[¶,24] For magnetics, SOC is very important since, in heterospin salts of the discussed RAs (see below), it can lead to spin canting *via* the Dzyaloshinsky–Moriya mechanism, *i.e.* to the ferrimagnetic ground state under conditions of antiferromagnetic (AF) exchange interactions between paramagnetic centers.[24]

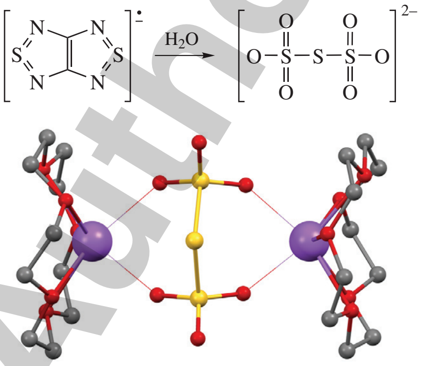

Figure 3 Hydrolysis of the 1,2,5-thidiazolidyl salt and the XRD structure of its product. Cation: $[Na(15\text{-crown-}5)]^+$.

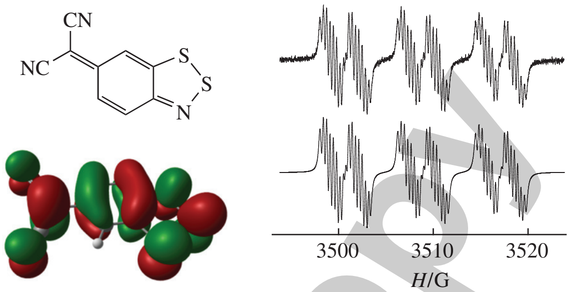

Figure 4 1,2,3-Dithiazole, the π*-SOMO, and the EPR spectrum (experiment and simulation) of its RA.

For a benzo-fused 1,2,3-dithiazole, the RA generated both electrochemically and chemically was detected by EPR. According to DFT, it possessed π*-SOMO (Figure 4).[4(b)] For other variously fused 1,2,3-dithia- and thiaselenazoles, electrochemical reduction was irreversible and RAs were not observed.[10(a),13(a)] DFT calculations suggested that their RAs unprecedentedly belonged to two types featuring normal and abnormal elongation of the S1–E2 (E = S or Se) bond, as compared with neutral precursors and possessing π*- and σ*-SOMOs, respectively.[13(a)]

The spin density on the van der Waals (VdW) surfaces of the discussed RAs is mostly positive; therefore, AF exchange interactions in the spin systems of their homospin salts should dominate according to the McConnell I model.[††,25] For a ferromagnetic (FM) ground state, contacts of unlike spin density are necessary requiring heterospin salts with negatively spin-polarized cations, which can be metal sandwich cations (see below).[4(a),5(b),15]

Radical-anion salts

Chemical reduction with various agents allowed one to synthesize both homospin (only anion is paramagnetic) and heterospin (both ions are paramagnetic) RA salts of the discussed heterocycles. Most of the salts were characterized by XRD.[21,22,26] Thermally stable homospin RA salts were obtained with elemental K, $[PhE]^-$ (E = S, Se), $(Me_2N)_2C{=}C(NMe_2)_2$ and $Co(\eta^5\text{-}C_5R_5)_2$ (R = H, Me) as reducing agents; the cations in the salts were $[K(THF)]^+$, $[K(18\text{-crown-}6)(L)]^+$ (L = –, MeCN), $[Na(15\text{-crown-}5)]^+$, $[Li(12\text{-crown-}4)_2]^+$, $[(Me_2N)_3S]^+$, $[(Me_2N)_2C{-}C(NMe_2)_2]^{2+}$ and $[Co(\eta^5\text{-}C_5R_5)_2]^+$.[19(e)–(j),20(a),26] The most interesting are salts revealed π-stacked (connected by pancake bonds)[27] RAs with shortened interplanar separation in the solid state (Figure 5),[21(g),22(a)] as well as salt for which co-packing of RAs and π-stacked units composed of RA and its neutral precursor was observed.[26] In the crystal, one of the salts shown in Figure 5 is EPR silent, whereas another is EPR active (both salts in solution are EPR active due to the fast dissociation of π-dimers).[21(g),22(a)] According to multiconfiguration CASSCF calculations for the EPR silent salt, the largest contributor to the singlet ground state of its π-dimers is a closed-shell electronic configuration, although the contribution

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[¶] The strength of the SOC involved in the Dzyaloshinsky–Moriya mechanism increases sharply with the atomic number *Z* as Z^4 to be efficient for atoms with *Z* > 30 (for S, Se and Te, *Z* = 16, 34, and 52, respectively).

[††] Spin polarization involved in the McConnell I mechanism is a real property, a positive spin density means that the associated magnetic moment is parallel to the net spin moment of the molecule and a negative spin density that the moments are antiparallel.

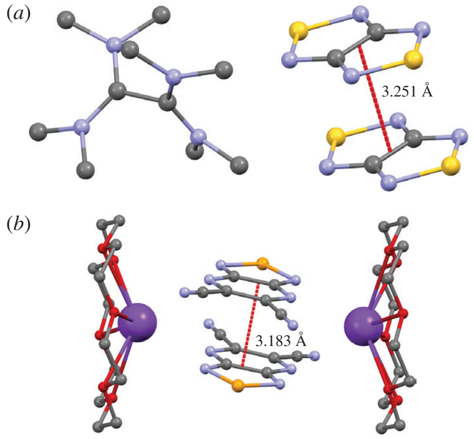

Figure 5 EPR (*a*) silent and (*b*) active salts featuring π-dimers of RAs in the crystal. Cations: (*a*) $[(Me_2N)_2C{-}C(NMe_2)_2]^{2+}$ and (*b*) [K(18-crown-6)]$^+$. Color codes: C, grey; K, purple; N, blue; O, red; S, yellow; and Se, orange (H omitted for clarity).

of a configuration with a singlet diradical character should also be accounted.[21(g)] In-depth investigation of the EPR active salt[22(a)] is in progress.

Thermally stable heterospin salts were synthesized with $Cr(\eta^5\text{-}C_5Me_5)_2$, $Cr(\eta^6\text{-}Ar)_2$ (Ar = benzene or toluene) and $Mo(\eta^6\text{-}Mes)_2$ (Mes = 1,3,5-trimethylbenzene) (Figure 6). An approach based on metal sandwich compounds is promising since it potentially covers 3*d*–5*d* and 4*f* metals.[5(b),15,28] As mentioned above, heavy metal atoms possessing Z^4-dependent strong SOC are very important for the design of new magnetics with the Dzyaloshinsky–Moriya spin-canting model (*d*-block: $Z = 24$, 42 and 74 for Cr, Mo and W, respectively)[¶,24] and for the design of the FM ground state of the heterospin salts with the McConnell I model[††,25] since, in some cases, their sandwich cations feature negative spin density on the VdW surfaces.[4(a),5(b),15]

Magnetic properties of the synthesized RA salts, which represent a new class of paramagnetics, were studied experimentally by SQUID magnetometry in a temperature range of 2–300 K and theoretically by quantum chemical calculations at various levels of theory (from broken-symmetry DFT to multiconfiguration CASSCF and NEVPT2) performed for their XRD structures. Generally, the magnetic motifs of salts were complex with RAs as multidentate magnetic couplers involved in numerous AF and FM exchange interactions. In both homo- and heterospin RA salts, the AF interactions dominated over the FM ones at cryogenic Neel temperatures.[15,21,26]

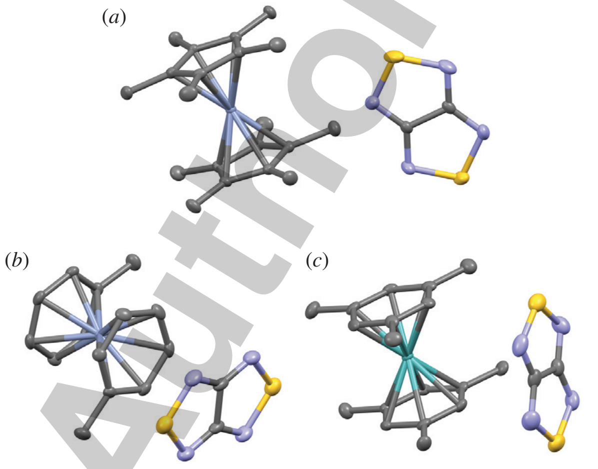

Figure 6 XRD structures of selected heterospin RA salts. Cations: (*a*) $[Cr(\eta^5\text{-}C_5Me_5)_2]^+$, (*b*) $[Cr(\eta^6\text{-}Tol)_2]^+$, and (*c*) $[Mo(\eta^6\text{-}Mes)_2]^+$. Color codes: C, grey; N, blue; and S, yellow (H omitted for clarity).

Charge-transfer complexes

1,2,5-Chalcogenadiazoles as electron acceptors form CT complexes with such electron donor as tetrathiafulvalene (TTF; Figure 7).[14(d)] Whereas thiadiazole complexes have normal 1 : 1 DA stoichiometry, and telluradiazole ones have 1 : 2 stoichiometry reflecting their propensity to form self-associates. The complexes display CT bands in the visible region of the electronic absorption spectra (VIS spectra), whose nature is confirmed by TD-DFT calculations, and the CT value (Mulliken) is about 0.2 e per molecule. In the solid state, the complexes are semiconductors with an activation energy of 0.3–0.4 eV, whose conductivity increases under white-light irradiation making them interesting for photovoltaics.[14(d)] Investigation of other CT complexes between 1,2,5-chalcogenadiazoles (S, Se, and Te) and TTF and its derivatives is in progress.

In the 2,1,3-benzochalcogenadiazole series, substitution in carbocycles provides the fine tuning of both EA_1 and the first ionization energy (IE_1).[‡‡,4(e),14(c)] This makes it possible to synthesize CT complexes of a new type where both electron donor and acceptor are 1,2,5-chalcogenadiazoles (Figure 8). These complexes are more weakly bonded than the above ones despite the fact that the Hirshfeld surface (HS) analysis accompanied by DA bonding energy portioning[29] disclosed numerous interactions between their components.[4(e)] The CT bands of the complexes are observable only in the solid-state VIS spectra and unobservable in solution spectra. Accordingly, the CT values (Mulliken) vary in a range of 0.02–0.03 e.[4(e),14(c)] In addition to the CT complexes, an unprecedented addition reaction was found for 1,2,5-chalcogenadiazole donor and acceptor (Figure 9). According to XRD and HS analysis of the reaction product, regular hexagonal voids share 40% of the unit cell volume. As a result, the product has an unusual porous structure, a kind of metal-free organic framework.[4(e)]

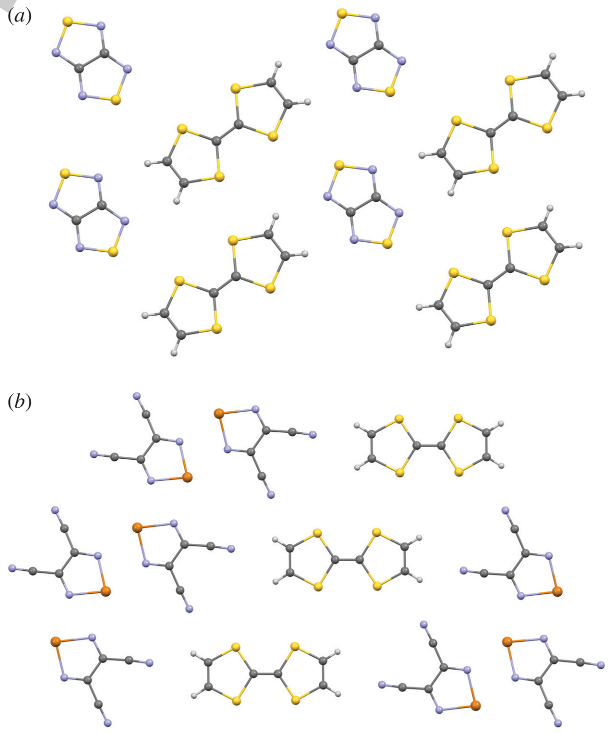

Figure 7 XRD structures of CT complexes between 1,2,5-chalcogenadiazoles and TTF, single layers are shown. Color codes: C, grey; H, white; N, blue; S, yellow; and Te, orange.

[‡‡] According to the Koopmans theorem, valid in the SCF theory and invalid in DFT one, IE_1 and EA_1 are equal to the HOMO and LUMO energies, respectively, taken with the opposite signs.

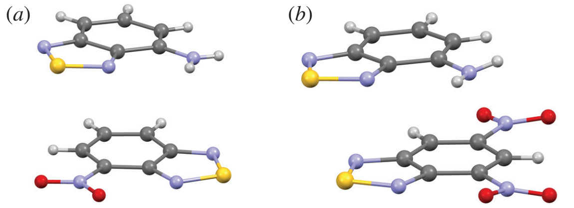

Figure 8 XRD structures of CT complexes between 4-amino-2,1,3-benzothiadiazole and (*a*) 4-nitro- and (*b*) 4,6-dinitro-2,1,3-benzothiadiazoles. Color codes: C, grey; H, white, N, green; O, red; and S, yellow.

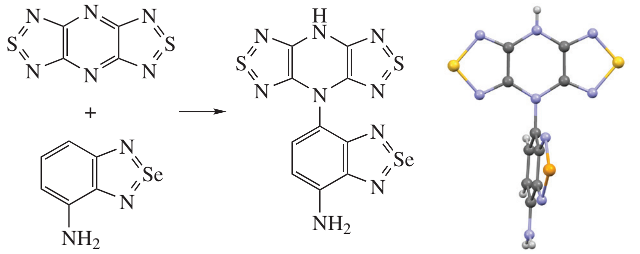

Figure 9 The addition reaction between bis(1,2,5-thiadiazolo)pyrazine (formal acceptor) and 4-amino-2,1,3-benzoselenadiazole (formal donor), and XRD structure of its product. Color codes: C, grey; H, white, N, green; O, red; S, yellow; and Se, orange.

Donor–acceptor complexes

1,2,5-Chalcogenadiazoles form DA complexes with neutral (N-heterocyclic carbenes – NHCs, pyridine, and DMSO) and charged (halides, pseudo halides, chalcogenolates, and oligotellurides) Lewis bases (Figure 10).[4(*f*),(*g*),16(*b*),22,30,31] In the latter case, the heterocycles act as anion receptors, which is a hot topic.[32] Note that the simultaneous coordination of two halides to a telluradiazole molecule was observed.[30(*d*)] The complexes reveal CT bands in the VIS spectra whose detection can, in principle, be used for anion sensing.[4(*f*),31(*b*)] The DA bonding energies depend strongly on the nature of both chalcogens and Lewis bases. The Te and Se derivatives form DA complexes with the anions more effectively than the S analogues, which correlate with the EA_1 of heterocycles (see above); complexes with neutral bases are known only for telluradiazoles. The DA bonding energies vary in a range of 25–85 kcal mol^{-1} for the anions (the lower value can be compared with the energy of the internal N–N bond in organic azides, and the higher, with that of C–C bond in alkanes) or 16–25 kcal mol^{-1} for the NHCs. The CT values (Mulliken) from Lewis bases onto heterocyclic moieties are 0.3–0.5 e for the halides, pseudo halides, and chalcogenolates; 0.8 e for $[Te_2]^{2-}$ and $[Te_4]^{2-}$; and 0.2–0.3 e for the NHCs.[4(*f*),(*g*),30,31]

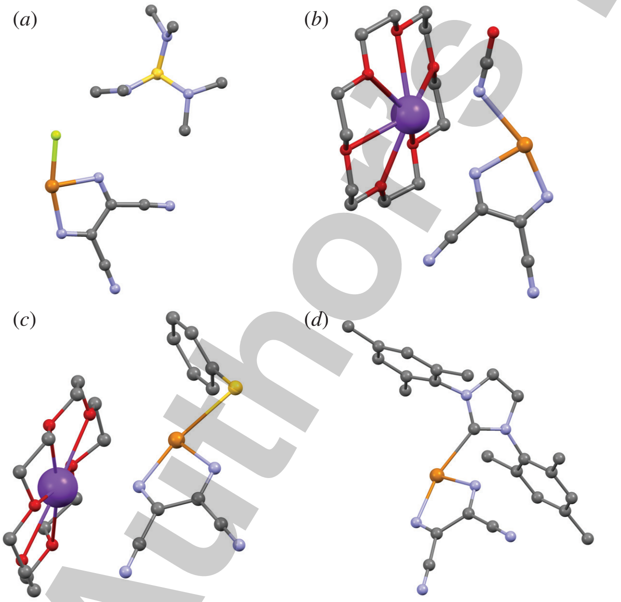

Figure 10 XRD structures of DA complexes between 3,4-dicyano-1,2,5-telluradiazole and (*a*) fluoride, (*b*) cyanate, (*c*) thiophenolate, and (*d*) NHC. Cations: (*a*) $[(Me_2N)_3S]^+$, (*b*) and (*c*) $[K(18\text{-crown-}6)]^+$. Color codes: C, grey; F, green; K, purple; N, blue; O, red; S, yellow; and Te, orange (H omitted for clarity).

According to XRD data, the DA bonds in all isolated complexes are longer than the sum of the covalent radii and shorter than the sum of the VdW radii of bonded atoms. According to DFT and NBO calculations and QTAIM analysis, as well as some modern descriptors,[30(*a*)] the DA bonds are formed by negative hyperconjugation, *i.e.* by CT from the MO of the lone pair of a Lewis base onto the virtual σ*-MO of the E–N bond of heterocycle (E = Te, Se, and S).[4(*g*),30,31] According to QTAIM, electron densities at bond critical points (BCPs) of the DA bonds are low (0.024–0.106 a.u.), and the values of an electron density Laplacian at the BCPs are positive, together indicating closed-shell (predominantly electrostatic) interactions.[4(*f*),(*g*),30]

Due to the wide disparity in the energies of the DA bonding between 1,2,5-chalcogenadiazoles and anions, the heterocycles are promising for the selective complexation of specific anions under competitive conditions. Indeed, for a mixture of 3,4-dicyano-1,2,5-telluradiazole with F^- and $SeCN^-$, the selective formation of a DA complex with F^- was detected by variable-temperature multinuclear NMR spectroscopy. However, this telluradiazole as an anion receptor is not so efficient as trimeric perfluoro-*ortho*-phenylenemercury (anticrown).[19] At least, from its mixture with $SeCN^-$ and anticrown, an anionic complex with the latter was isolated and structurally characterized by XRD analysis.[4(*f*)]

Metal coordination compounds

2,1,3-Benzothia(selena)diazoles are ligands in coordination compounds of metals including Mn, Fe, Co, Ni, Cu, Zn, Ag, Cd, Ir, Hg, Dy, Er, and Yb.[17,33] The coordination chemistry of their Te congeners is not developed. The same is also true for closed-shell neutral 1,2,3-dichalcogenazoles, whereas the metal complexes of 1,2,3-dithiazolyls and their Se analogues are known.[34] The thia(selena)diazole complexes revealed a number of coordination modes. Notably, the heterocyclic N atom was a coordination center even in the presence of the NH_2 group in carbocycle, whereas the OH group led to a chelate structure (Figure 11).[17(*b*)] More sophisticated carbocyclic functionalization provides additional coordination facilities.[17,33]

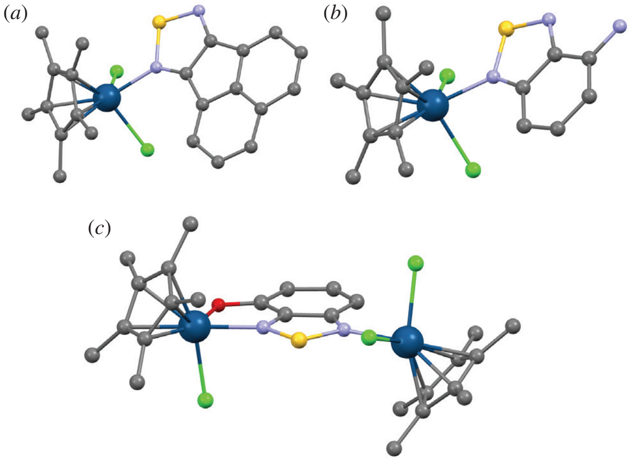

Figure 11 XRD structures of Ir complexes with 1,2,5-thiadiazole ligands featuring different coordination modes: (*a*) monodentate coordination and (*b*) its retention in the presence of NH_2 group, and (*c*) chelating coordination in the presence of OH group. Color codes: C, grey; Cl, light green; Ir, deep green; N, blue; and S, yellow (H omitted for clarity).

The complexes synthesized revealed interesting photophysical and magnetic properties with paramagnetic cations. Particularly, the heteroligand tetranuclear complexes of Er and Yb displayed luminescence in the near IR (NIR) region. The luminescence intensity increased with the number of the thiadiazole ligands suggesting them as a new effcient antenna ligand for the lanthanide-based NIR luminescence.[33(*b*),(*d*)] The complexes of Cd revealed red luminescence.[33(*c*)]

Conclusions

The charge-transfer properties of the chalcogen–nitrogen π-heterocycles are promising for both chemistry and materials science. In the context of donor–acceptor complexes, these properties belong to chalcogen bonds/interactions[35] (*cf.* halogen bonds)[36] received much current attention. Note that they are a useful tool for the synthesis of new compounds featuring hardly accessible bonds between two different chalcogens. Although interchalcogen bonds are relatively weak, they are important for physical, chemical, and biological processes, including the transfer of chiral information in chemical reactions.[37] With 1,2,5-chalcogenadiazoles, the discussed charge-transfer chemistry can be expanded onto their 1-oxides,[38] with radical anions onto lanthanide complexes.[28] For 1,2,3-dithiazoles, special prospects are associated with the self-condensation of Herz radicals into polycyclic derivatives[39] – ligands for metal coordination compounds and the precursors of radical anions, radical-anion salts, and charge-transfer and donor–acceptor complexes. Many other chalcogen–nitrogen π-heterocyclic systems can be potentially involved in the charge-transfer chemistry;[4(*a*)] the most interesting are heavier chalcogen derivatives. In the materials science context, it is likely that the radical anions and radical-anion salts of the discussed heterocycles are mainly of fundamental significance due to their air sensitivity. However, the charge-transfer and donor–acceptor complexes and metal coordination compounds (especially those of lanthanides) can find real practical applications in the design and synthesis of smart materials.[§§,40]

As compared with the charge-transfer chemistry of 1,2,5-chalcogenadiazoles, that of their acyclic analogs R–N=E=N–R is a missing link despite they are redox-active (E = S)[28,41] and their radical-anion complexes with lanthanides (E = S)[28] and interactions with anions (E = S, Se, Te) are known (in contrast to the heterocycles, the reactions with anions proceed as addition to the E=N bonds).[42] One can think that the expansion of the discussed charge-transfer heterocyclic chemistry onto relevant acyclic compounds will be useful.

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[§§] By definition, smart materials are designed materials possessing one or more properties which can be significantly changed in controlled mode by external impact, *e.g.* magnetic field (molecular magnets), light (molecular photoconductors), chemical compounds (molecular sensors), *etc*.

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