

atom involved in the electron-acceptor component. This bonding description is still common in current studies, but is dominant for the strongest interactions, whereas an electrostatic model for the interactions first advanced 15 years ago, and usually referred to as the σ -hole model (Clark *et al.*, 2007; Politzer *et al.*, 2013), is generally thought to provide the best description of weak to moderate strength interactions. Indeed, the electrostatic description has become sufficiently prevalent that this class of interactions is often referred to as σ -hole interactions, as we have done in the title of this article, although the term perhaps lacks universality since it implies a universal (electrostatic) bonding model. Alcock's earlier term *secondary bonding* is not prescriptive, but refers to interactions other than primary (covalent) bonds. Subclasses of interactions involving elements from a particular p -block group in the Lewis acidic role are most commonly named after the class of elements that comprise the group, the most common being halogen bonds (Group 17), chalcogen bonds (Group 16), pnictogen bonds (Group 15) and tetrel bonds (Group 14). In a tutorial review entitled '*Hypervalency, secondary bonding and hydrogen bonding: siblings under the skin*,' which also benefits from some historical perspective, Crabtree (2017) provides an important reminder that there is a continuum of behaviour, both in geometry and bonding description, from weak secondary bonding through to the strongest interactions that evolve into hypervalency of the main group elements. This continuum description applies equally to hydrogen bonding.

After a period of relative dormancy, the field of halogen bonding has grown enormously in the past 25 years, accelerated initially by studies in the late 1990s/early 2000s that made clear the similarities between halogen bonding and the more widely studied hydrogen bonding, notably the matrix-isolation and gas-phase rotational spectroscopy studies of Legon and co-workers (Legon, 1999), and the introduction by Resnati, Metrangolo and colleagues of perfluoroalkyl and -aryl halides to enable strong directional halogen bonding in the condensed phases (Corradi *et al.*, 2000). The evolution of halogen bonding is such that not only are there many reviews on this topic (*e.g.* Metrangolo *et al.*, 2005; Rissanen, 2008; Brammer *et al.*, 2008; Fourmigué, 2009; Cavallo *et al.*, 2010; Bertani *et al.*, 2010; Parisini *et al.*, 2011; Erdélyi, 2012), but many reviews even focus on specific applications of halogen bonding (Section 2.1). Chalcogen bonds are the next most widely studied class of secondary bonding interactions, their under-

standing and application having advanced considerably in the past decade. Reviews that focus specifically on these or the other classes of interactions are now also plentiful. Thus, we have endeavoured to bring together a compilation of the many topics that have been reviewed in the sections below, along with tabulated and categorized lists of reviews [including survey articles in which the Cambridge Structural Database (CSD; Groom *et al.*, 2016) has been used as the primary source of experimental data to identify interactions, and reviews that include new computational studies of the compounds being surveyed]. The aim has been to provide an ease of departure into the extensive literature on the classes of interactions (Fig. 1) that are brought together in this special issue of *Acta Crystallographica Section C: Structural Chemistry*.

2. Signposting reviews on secondary bonding: halogen bonds, chalcogen bonds, pnictogen bonds, tetrel bonds, etc.

In the following sections, we have very briefly summarized the broad areas covered by reviews on each class of secondary bonding interactions. Although a comprehensive list would be desirable, accomplishing this with certainty is difficult to ensure. Given the vast number of reviews, we have focused on those published in the past decade (2013–present). There are, of course, several key reviews that precede this period. A selection of these is noted in the *Introduction* (Section 1). There will inevitably be reviews published that are not listed in Tables 1–5; their omission is unintentional. There are also a number of collections of articles in journals that have been compiled around this topic. A good example is the series of articles associated with the 203rd Faraday Discussion meeting on '*Halogen Bonding in Supramolecular and Solid State Chemistry*,' held in Ottawa, Canada, on 10–12th July, 2017 (see, for example, Clark, 2017; Brammer, 2017), which includes transcripts of the extensive discussion arising from the presented articles (Aakeröy *et al.*, 2017*a,b,c,d*). Section 3 (*vide infra*) provides an overview of the collection of articles in the special issue of this journal, with which the present article is associated.

2.1. Reviews of halogen bonding

As noted in the *Introduction* (Section 1), halogen bonding was the first of the σ -hole interactions to receive renewed

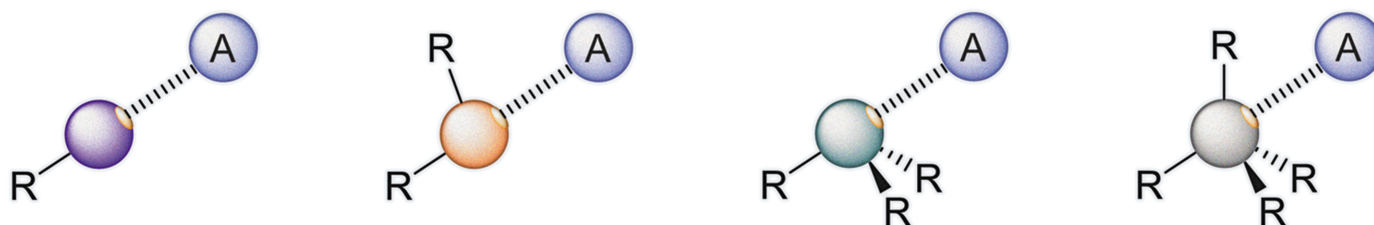


Figure 1

Left to right: halogen bond, chalcogen bond, pnictogen bond and tetrel bond. Each p -block atom is shown with its most common number of substituents (R) engaging in an intermolecular (σ -hole) interaction with a Lewis basic acceptor group (A).

Table 1

List of reviews on halogen bonding since 2013.

Title	Reference
General	
Metal Centers as Nucleophiles: Oxymoron of Halogen Bond-Involving Crystal Engineering	Ivanov <i>et al.</i> (2022)
Words in supramolecular chemistry: the ineffable advances of polyiodide chemistry	Savastano (2021)
The Halogen Bond	Cavallo <i>et al.</i> (2016)
Halogen Bonding in Hypervalent Iodine Compounds	Catalano <i>et al.</i> (2016)
Halogen Bonding in Supramolecular Chemistry	Gilday <i>et al.</i> (2015)
Halogen bonding I: Impact on materials chemistry and life sciences	Cavallo <i>et al.</i> (2015)
Halogen bonding II: Impact on materials chemistry and life sciences	Kolář <i>et al.</i> (2015)
Theoretical perspectives	
Application of Halogen Bonding to Organocatalysis: A Theoretical Perspective	Yang & Wong (2020)
Charge Displacement Analysis – A Tool to Theoretically Characterize the Charge Transfer Contribution of Halogen Bonds	Ciancaleoni <i>et al.</i> (2020)
Modern level for properties prediction of iodine-containing organic compounds: the halogen bonds formed by iodine	Bartashevich <i>et al.</i> (2017)
Computer Modelling of Halogen Bonds and Other σ -Hole Interactions	Kolář & Hobza (2016)
The many faces of halogen bonding: a review of theoretical models and methods	Wolters <i>et al.</i> (2014)
Interplay between non-covalent interactions in complexes and crystals with halogen bonds	Bartashevich & Tsirelson (2014)
Halogen bonds in solids	
Recent Progress of Noncovalent Interaction-Driven Self-Assembly of Photonic Organic Micro/Nanostructures	Ma <i>et al.</i> (2022)
Crystal engineering strategies towards halogen-bonded metal–organic multi-component solids: salts, cocrystals and salt cocrystals	Nemec <i>et al.</i> (2021)
Characterizing Supramolecular Architectures in Crystals Featuring I...Br Halogen Bonding: Persistence of $X \cdots X'$ Secondary-Bonding in Their Congeners	Tiekink (2021a)
Halogen bonding in the co-crystallization of potentially ditopic diiodotetrafluorobenzene: a powerful tool for constructing multicomponent supramolecular assemblies	Ding <i>et al.</i> (2020)
Halogen Bonding: A Halogen-Centered Noncovalent Interaction Yet to Be Understood	Varadwaj <i>et al.</i> (2019)
From Molecules to Interactions to Crystal Engineering: Mechanical Properties of Organic Solids	Saha <i>et al.</i> (2018)
Molecular Recognition with Resorcin[4]arene Cavitands: Switching, Halogen-Bonded Capsules, and Enantioselective Complexation	Gropp <i>et al.</i> (2018)
Co-crystallization of 1,3,5-trifluoro-2,4,6-triiodobenzene (1,3,5-TFTIB) with a variety of Lewis bases through halogen-bonding interactions	Ding <i>et al.</i> (2017)
Crystallography of encapsulated molecules	Rissanen (2017)
Halogen bonding: A powerful, emerging tool for constructing high-dimensional metal-containing supramolecular networks	Li <i>et al.</i> (2016)
Halogen Bonds in Crystal Engineering: Like Hydrogen Bonds yet Different	Mukherjee <i>et al.</i> (2014)
Alternative Motifs for Halogen Bonding	Troff <i>et al.</i> (2013)
The Halogen Bond in the Design of Functional Supramolecular Materials: Recent Advances	Priimagi <i>et al.</i> (2013)
Halogen bonds on surfaces	
Halogen Bonds Fabricate two-dimensional Molecular Self-Assembled Nanostructures by Scanning Tunneling Microscopy	Wang <i>et al.</i> (2020b)
Halogen Bonding in Two-Dimensional Crystal Engineering	Teyssandier <i>et al.</i> (2020)
Halogen bonds in solution and gas phase	
Halogen bonding motifs for anion recognition	Pancholi & Beer (2020)
Halogen bonds of halonium ions	Turunen & Erdélyi (2020)
Halogen bonding in solution: NMR spectroscopic approaches	von der Heiden <i>et al.</i> (2020)
The Hydrogen Bond, the Halogen Bond and Rotational Spectroscopy: A Personal Retrospective	Legon (2020)
Helical Anion Foldamers in Solution	John <i>et al.</i> (2020)
Halogen Bonding in Solution: Anion Recognition, Templated Self-Assembly, and Organocatalysis	Tepper & Schubert (2018)
Characterization of Halogen Bonded Adducts in Solution by Advanced NMR Techniques	Ciancaleoni (2017)
Anion Recognition Strategies Based on Combined Noncovalent Interactions	Molina <i>et al.</i> (2017)
Halogen bond symmetry: the N–X–N bond	Hakkert & Erdélyi (2015)
Advances in Anion Supramolecular Chemistry: From Recognition to Chemical Applications	Evans & Beer (2014)
Halogen bonding in solution: thermodynamics and applications	Beale <i>et al.</i> (2013)
Applications: materials/synthesis	
Halogen bonding regulated functional nanomaterials	Zheng <i>et al.</i> (2021)
Non-covalent interactions (NCIs) in π -conjugated functional materials: advances and perspectives	Haque <i>et al.</i> (2023)
Stereoselective Processes Based on σ -Hole Interactions	Peluso & Mamane (2022)
Halogen Bonding in Perovskite Solar Cells: A New Tool for Improving Solar Energy Conversion	Metrangolo <i>et al.</i> (2022)
Halogen bonding in polymer science: towards new smart materials	Kampes <i>et al.</i> (2021)
Bridging the Void: Halogen Bonding and Aromatic Interactions to Program Luminescence and Electronic Properties of π -Conjugated Materials in the Solid State	Sharber <i>et al.</i> (2021)
Halogen bond-induced electrophilic aromatic halogenations	Lorpaiboon & Bovonsombat (2021)
An up-to-date review on halogen-bonded liquid crystals	Devadiga & Ahipa (2021)
Halogen bonding in room-temperature phosphorescent materials	Wang <i>et al.</i> (2020a)
Organic halogen-bonded co-crystals for optoelectronic applications	Chen <i>et al.</i> (2020)
Supramolecular Halogen Bonds in Asymmetric Catalysis	Kaasik & Kanger (2020)
Recent Advances in Halogen Bond-assisted Organic Synthesis	Yamada & Konno (2020)

Table 1 (continued)

Title	Reference
Enhanced Room-Temperature Phosphorescence through Intermolecular Halogen/Hydrogen Bonding	Xiao & Fu (2019)
Halogen Bonding beyond Crystals in Materials Science	Saccone & Catalano, (2019)
Electrochemical activation of halogen bonding	Fave & Schöllhorn (2019)
Halogen-Bonded Cocrystals as Optical Materials: Next-Generation Control over Light-Matter Interactions	Christopherson <i>et al.</i> (2018)
Halogen bonding in polymer science: from crystal engineering to functional supramolecular polymers and materials	Berger <i>et al.</i> (2015)
Halogen bonding at work: recent applications in synthetic chemistry and materials science.	Meyer & Dubois (2013)
Biomolecules	
Noncovalent interactions in proteins and nucleic acids: beyond hydrogen bonding and π -stacking	Jena <i>et al.</i> (2022)
A Halogen Bonding Perspective on Iodothyronine Deiodinase Activity	Marsan & Bayse (2020)
Halogen Bonding in Biomimetic Deiodination of Thyroid Hormones and their Metabolites and Dehalogenation of Halogenated Nucleosides	Mondal <i>et al.</i> (2020b)
Halogen Bonding in the Molecular Recognition of Thyroid Hormones and Their Metabolites by Transport Proteins and Thyroid Hormone Receptors	Mondal <i>et al.</i> (2020a)
Hydrogen Bond Enhanced Halogen Bonds: A Synergistic Interaction in Chemistry and Biochemistry	Riel <i>et al.</i> (2019)
Directing Traffic: Halogen-Bond-Mediated Membrane Transport	Govindaraj <i>et al.</i> (2019)
Halogen bonding in halocarbon–protein complexes and computational tools for rational drug design	Costa <i>et al.</i> (2019)
Looking Back, Looking Forward at Halogen Bonding in Drug Discovery	Mendez <i>et al.</i> (2017)
Halogen bonds involved in binding of halogenated ligands by protein kinases	Poznański <i>et al.</i> (2016)
Molecular Recognition in Chemical and Biological Systems	Persch <i>et al.</i> (2015)
Synthetic Ion Transporters that Work with Anion– π Interactions, Halogen Bonds, and Anion–Macrodipole Interactions	Vargas Jentzsch <i>et al.</i> (2013)
Halogen bonding (X-bonding): A biological perspective	Scholfield <i>et al.</i> (2013)

attention in the revival and blossoming of research over the past 25-plus years; it remains the most widely studied of these related interactions. This has led to a large number of reviews within the past ten years (Table 1) and has even resulted in the publication of a number of books focusing on halogen bonding (Cavallo *et al.*, 2015; Kolář *et al.*, 2015).

Reviews cover halogen bonding in the solid state, in solution and in the gas phase. A simple overview of the developing trends within these reviews reveals that, within the past decade, the focus has shifted from the general reviews that dominated the first half of the decade to reviews focusing on furthering the understanding of halogen bonding, *e.g.* utilizing computational input, with reviews centred on specific applications of halogen bonding becoming more prominent in the latter half of the past decade. This snapshot of the field illustrates the promise for the use of halogen bonding in a variety of applications and fields, including materials chemistry, organocatalysis and biologically/medically relevant areas. These trends towards employing halogen bonding to modify the properties of materials or the reactivity/activity of molecules are echoed in the reviews of the related interactions, alluding to the role that σ -hole interactions will play in future scientific research. Lists of reviews on chalcogen bonding, pnictogen bonding and tetrel bonding are provided in Tables 2–5.

2.2. Reviews of chalcogen bonding

In this section, a collection of reviews that are related specifically to chalcogen bonding is provided. A list of these reviews can be found in Table 2. Although these reviews focus primarily on the supramolecular and crystal engineering aspects of the chalcogen bond, areas such as drug development and biological aspects, as well as materials chemistry, are also prevalent. Furthermore, the role of chalcogen bonding in

organic synthesis and catalysis is covered in several of the listed reviews. A reader unfamiliar with the topic may find the overview of chalcogen bonding by Huber and co-workers a good starting point (Vogel *et al.*, 2019), while a general definition of the chalcogen bond has been provided through the IUPAC (International Union of Pure and Applied Chemistry) nomenclature process (Aakeröy *et al.*, 2019).

2.3. Reviews of pnictogen bonding

The reviews listed in Table 3 are those dedicated exclusively to pnictogen (also pnicogen) bonding and cover this particular σ -hole interaction mainly from a crystal engineering point of view, but also review the fundamental aspects of the pnictogen bond by summarizing articles that involve relevant computational results. To highlight some of these reviews, Varadwaj and co-workers provide four separate reviews (Varadwaj *et al.*, 2022b,c,d,e, 2023b), each devoted to a specific atom of the pnictogen family and its respective pnictogen-bonded systems, based on crystal structures present in the Cambridge Structural Database (CSD). Furthermore, a CSD survey of coordination and organometallic compounds which involve pnictogen-bond motifs has been conducted by Mahmudov *et al.* (2022), while the review by Scheiner (2013b) provides a comprehensive look at the fundamental aspects of the pnictogen bond. The significance of pnictogen bonding in areas such as catalysis and biology are highlighted in reviews listed in Table 5 that focus on multiple types of σ -hole interactions.

2.4. Reviews of tetrel bonding

Similar to pnictogen bonding, the reviews of tetrel bonding listed in Table 4 concentrate largely in surveying crystallographic data using the CSD, while some of these reviews provide a comprehensive look at the characteristic features of the tetrel bond by drawing conclusions mainly from com-

sigma-hole interactions

Table 2

List of reviews on chalcogen bonding since 2013.

Te···N secondary-bonding interactions in tellurium crystals: Supramolecular aggregation patterns and a comparison with their lighter congeners	Tiekink (2022)
Metal Coordination Enhances Chalcogen Bonds: CSD Survey and Theoretical Calculations	Frontera & Bauza (2022)
Chalcogen bonding in coordination chemistry	Mahmudov <i>et al.</i> (2022)
Harnessing noncovalent interaction of chalcogen bond in organocatalysis: From the catalyst point of view	Yan <i>et al.</i> (2021)
Supramolecular aggregation patterns featuring Se···N secondary-bonding interactions in mono-nuclear selenium compounds: A comparison with their congeners	Tiekink (2021 <i>b</i>)
Zero-, one-, two- and three-dimensional supramolecular architectures sustained by Se···O chalcogen bonding: A crystallographic survey	Tiekink (2021 <i>c</i>)
Participation of S and Se in hydrogen and chalcogen bonds	Scheiner (2021)
Chalcogen bonding in materials chemistry	Ho <i>et al.</i> (2020)
Chalcogen bonding in crystalline diselenides and selenocyanates: From molecules of pharmaceutical interest to conducting materials	Fourmigué & Dhaka (2020)
Chalcogen-bond driven molecular recognition at work	Biot & Bonifazi (2020)
Anion recognition using chalcogen bonding	Tanii (2020)
Chalcogen Bonding: An Overview	Vogel <i>et al.</i> (2019)
Dithienothiophenes at Work: Access to Mechanosensitive Fluorescent Probes, Chalcogen-Bonding Catalysis, and beyond	Strakova <i>et al.</i> (2019)
The Chalcogen Bond in Crystalline Solids: A World Parallel to Halogen Bond	Scilabra <i>et al.</i> (2019)
Secondary Forces in Protein Folding	Newberry & Raines (2019)
Adaptive responses of sterically confined intramolecular chalcogen bonds	Selvakumar & Singh (2018)
Molecular and supramolecular chemistry of mono- and diselenium analogues of metal dithiocarbamates	Lee <i>et al.</i> (2018)
Chalcogen bonding in synthesis, catalysis and design of materials	Mahmudov <i>et al.</i> (2017 <i>b</i>)

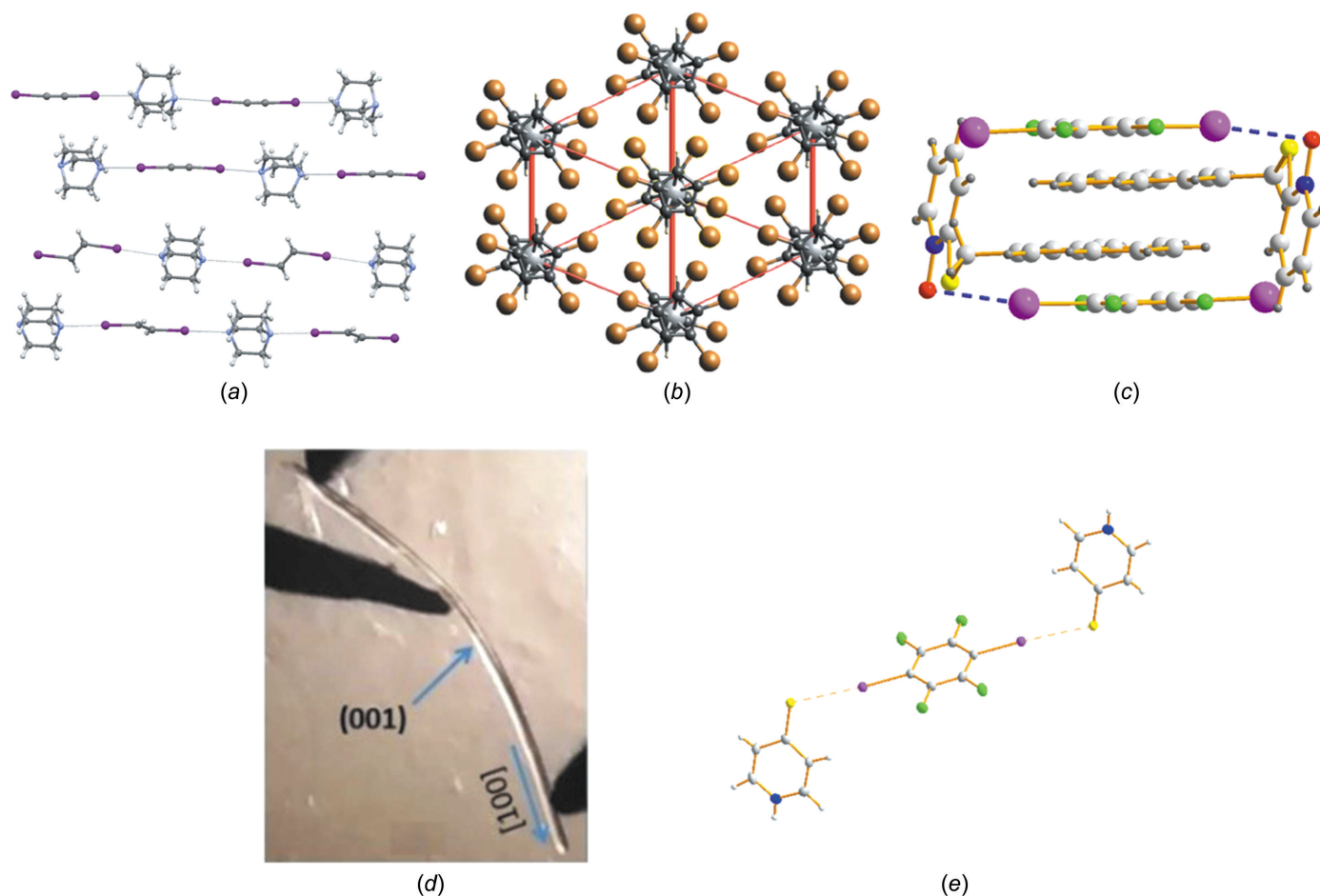


Figure 2

(a) C–I···N halogen bonding in the series C_2I_2 ·DABCO, $C_2H_2I_2$ ·DABCO and $C_2H_4I_2$ ·DABCO (Torubaev & Skabitskiy, 2022). (b) Polybromoferrocenes – multiple halogen-containing interactions (Blockhaus & Sünkel, 2022). (c) C–I···O halogen bonding and π -stacking in flexible NPTO (Wang *et al.*, 2023). (d) Bending crystals of 4-halobenzonitrile containing C–X···N \equiv C halogen bonds (Veluthaparambath *et al.*, 2022). (e) C–I···S halogen-bonded cocrystals – links to the nucleophilic substitution reaction (Mosquera *et al.*, 2023). All figures are reproduced from the cited references with permission.

Table 3

List of reviews on pnictogen bonding since 2013.

The Pnictogen Bond Forming Ability of Bonded Bismuth Atoms in Molecular Entities in the Crystalline Phase: A Perspective	Varadwaj <i>et al.</i> (2023b)
The Nitrogen Bond, or the Nitrogen-Centered Pnictogen Bond: The Covalently Bound Nitrogen Atom in Molecular Entities and Crystals as a Pnictogen Bond Donor	Varadwaj <i>et al.</i> (2022d)
The Phosphorus Bond, or the Phosphorus-Centered Pnictogen Bond: The Covalently Bound Phosphorus Atom in Molecular Entities and Crystals as a Pnictogen Bond Donor	Varadwaj <i>et al.</i> (2022e)
The Pnictogen Bond: The Covalently Bound Arsenic Atom in Molecular Entities in Crystals as a Pnictogen Bond Donor	Varadwaj <i>et al.</i> (2022b)
The Stibium Bond or the Antimony-Centered Pnictogen Bond: The Covalently Bound Antimony Atom in Molecular Entities in Crystal Lattices as a Pnictogen Bond Donor	Varadwaj <i>et al.</i> (2022c)
The Pnictogen Bond, Together with Other Non-Covalent Interactions, in the Rational Design of One-, Two- and Three-Dimensional Organic–Inorganic Hybrid Metal Halide Perovskite Semiconducting Materials, and Beyond	Varadwaj <i>et al.</i> (2022a)
Pnictogen bonding in coordination chemistry	Mahmudov <i>et al.</i> (2022)
Fluorinated elements of Group 15 as pnictogen bond donor sites	Scilabra <i>et al.</i> (2017)
The pnictogen bond: Its relation to hydrogen, halogen, and other noncovalent bonds	Scheiner (2013b)

putational studies or in conjunction with experimental data. Although not a review and therefore not listed in Table 4, a recent article by Varadwaj *et al.* (2023a) is worth mentioning here since it proposes a definition of the tetrel bond. Some of the listed surveys look mainly at C atoms as the Lewis acidic centre, although reviews focusing on tetrel bonding involving its heavier congeners germanium, tin and especially lead are also listed. We note that the review by Laplaza *et al.* (2021) is placed in Table 4 rather than Table 5 since the authors place tetrel bonds in particular focus while analysing ‘new bonding situations’ using the highlighted computational method (Laplaza *et al.*, 2021).

2.5. Reviews that include multiple σ -hole interaction types

Associating each review strictly with a single class of interaction (*i.e.* halogen, chalcogen, pnictogen or tetrel bonding) is not always possible and therefore in Table 5 we provide an extended list of reviews in which two or more of these σ -hole interactions are reviewed. This list also contains reviews that compare the features of tetrel, pnictogen, chalcogen and/or halogen bonding with hydrogen bonds. Additionally, some of these reviews provide further reading on other types of noncovalent interactions beyond the σ -hole interactions introduced above, including aerogen (noble gas)

bonding and triel (Group 13) bonding, as well as so-called π -hole interactions.

2.6. Other σ -hole or related interactions

Although this review and the accompanying special issue of the journal have focused on σ -hole interactions involving Group 14–17 elements in the Lewis acidic role, it has long been recognized that elements from other groups can also form analogous interactions. In most cases, these interactions are currently the subject of insufficient studies to warrant a review article. The involvement of noble gases in such secondary bonding interactions was reviewed by Alcock 50 years ago (Alcock, 1972). More recent work, under the classification of aerogen bonds has come from individual studies (*e.g.* Bauzá & Frontera, 2015). Interactions involving Group 13 elements as Lewis acids have been reviewed recently under the classification of triel bonds (Grabowski, 2020b). Lewis acidic behaviour, however, is already well established, *i.e.* typical behaviour, of Group 13 elements. The description of triel bonding for these elements relies on describing the well-established chemistry in terms of a π -hole interaction at the triel element. Analogies between the σ -hole description of interactions of Group 14–18 elements have also recently been evoked for weak interactions of Lewis bases with some tran-

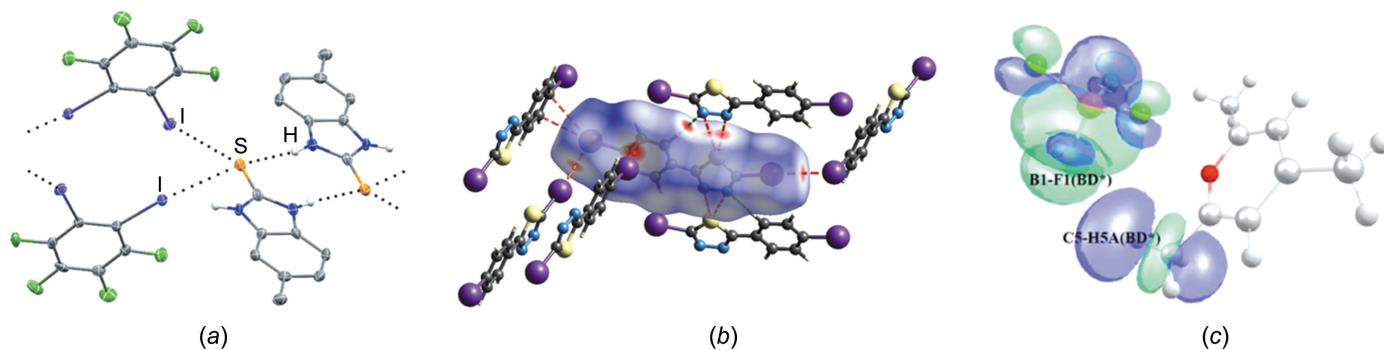


Figure 3

(a) C—I...S halogen bonding in organoiodine cocrystals of heterocyclic thiones (Watts *et al.*, 2022). (b) Competition between halogen and chalcogen bonds in halogen-bearing chalcogenadiazoles (De Silva *et al.*, 2022). (c) B—F...O and B—F...C interactions and orbital analysis in 2,4,6-trimethylpyrylium tetrafluoroborate (Mandal *et al.*, 2022). All figures are reproduced from the cited references with permission.

Table 4

List of reviews on tetrel bonding since 2013.

Recent advances on the tetrel bonding interaction in the solid state structure of lead complexes with hydrazine based bis-pyridine Schiff base ligands	Banerjee <i>et al.</i> (2022)
NCIPLOT and the analysis of noncovalent interactions using the reduced density gradient	Laplaza <i>et al.</i> (2021)
C(sp^3) atoms as tetrel bond donors: A crystallographic survey	Daolio <i>et al.</i> (2020)
Tetrel Bonding Interactions Involving Carbon at Work: Recent Advances in Crystal Engineering and Catalysis	Frontera (2020)
Tetrel bonding interactions at work: Impact on tin and lead coordination compounds	Bauzá <i>et al.</i> (2019)
Close contacts involving germanium and tin in crystal structures: experimental evidence of tetrel bonds	Scilabra <i>et al.</i> (2018)
Tetrel Bonding Interactions	Bauzá <i>et al.</i> (2016)

sition-metal complexes of Groups 7, 8, 11 and 12 (Daolio *et al.*, 2021*a,b*; Legon & Walker, 2018; Bauzá *et al.*, 2020; Banerjee *et al.*, 2022; Gomila & Frontera, 2022). Caution should perhaps be observed here so as not to reimagine all of *d*-block coordination chemistry in terms of σ -holes, but some structural and bonding analogies between weak interactions involving these *d*-block elements and those involving *p*-block elements is clearly of value. A survey of related interactions from across the *s*- and *p*-blocks, and part of the *d*-block has been reported by Alkorta *et al.* (2020).

3. The virtual special issue

The virtual special issue of this journal, which runs under the heading ‘Halogen, chalcogen, pnictogen and tetrel bonds: structural chemistry and beyond’ was conceived as providing a snapshot of current research activity and includes 11 articles that cover a variety of aspects associated with this class of interactions. There are articles that focus on structure, bonding and bond strength, articles that investigate co-operation or competition between different classes of interactions, articles that explore the relationship between these interactions and chemical or physical properties of the compounds and materials involved, and, although all articles involve characterization by single-crystal X-ray diffraction, a number have a prominent focus on other experimental techniques or are combined with interpretation from theoretical calculations.

Halogen bonding and chalcogen bonding dominate these articles, consistent with the wider literature (*vide supra*).

Five articles focus on different aspects of the structure, bonding and resulting properties of halogen-bonded crystals (Fig. 2). Torubaev & Skabitskiy (2022; see also Perkins *et al.*, 2012) use X-ray crystallography to study the effect on C—I \cdots N halogen bonds of the hybridization at the C atom across the series C₂I₂·DABCO, C₂H₂I₂·DABCO and C₂H₄I₂·DABCO (DABCO is 1,4-diazabicyclo[2.2.2]octane), demonstrating that, in these linear halogen-bonded assemblies, halogen-bond lengths (I \cdots N) follow the trend C(sp^2)—I \cdots N < C(sp^2)—I \cdots N < C(sp^3)—I \cdots N. The crystallographic results are supported by calculations of electrostatic potentials. Blockhaus & Sünkel (2022) report the synthesis of a series of highly brominated ferrocenes [C₁₀H_{10-n}Br_nFe], with *n* = 4–9. The crystal structures of some of these compounds are described and exhibit C—H \cdots Br hydrogen bonds, C—Br \cdots Br—C interactions, some of which are halogen bonds, and C—Br \cdots π halogen bonds. These compounds are discussed in the broader context of other polybromoferrocenes and other polyhaloferrocenes, and analysed using Hirshfeld surface representations and by intermolecular energy calculations. Wang, Wu and Jin report halogen-bonded cocrystals of di- and triiodoperfluorobenzenes with a flexible thioether containing a strong halogen-bond acceptor pyridyl *N*-oxide group (Wang *et al.*, 2023). Accommodation of the halogen-bond donor species in the cocrystals involves a change in conformation of the flexible NPTO molecule (NPTO is 2-[[naphthalen-2-yl)methyl]sulfanyl]

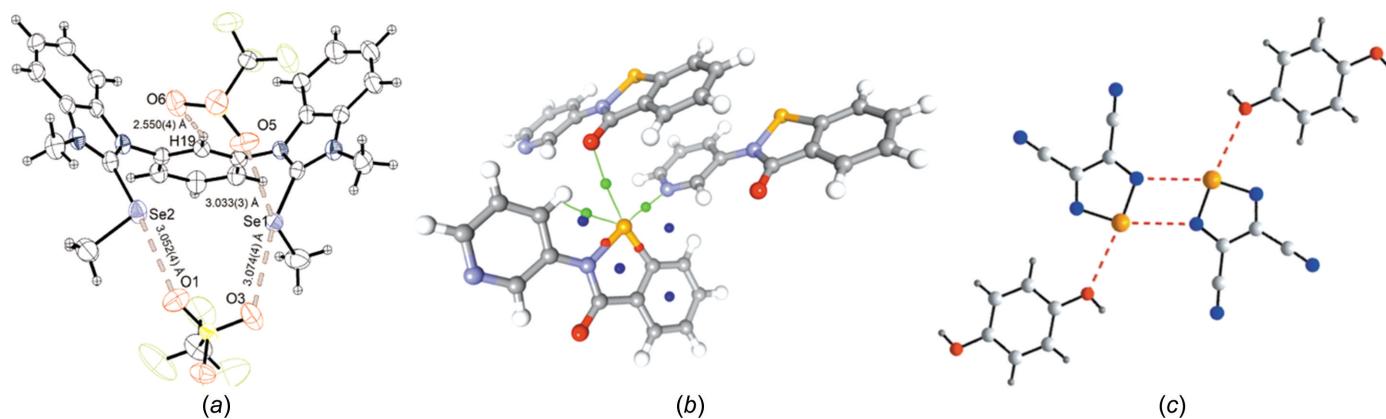


Figure 4

(a) C—Se \cdots O chalcogen bonding in 1,3-bis(benzimidazolium)benzene-based chalcogen-bonding catalysts (Steinke *et al.*, 2023). (b) C—Se \cdots N and C—Se \cdots O chalcogen bonding in ebsele analogues, shown with critical points in electron density (Xu *et al.*, 2023). (c) N—Ch \cdots N and N—Ch \cdots O chalcogen bonding in 3,4-dicyano-1,2,5-chalcogenodiazole cocrystals studied by solid-state NMR spectroscopy (Nag *et al.*, 2022). All figures are reproduced from the cited references with permission.

Table 5

List of reviews (since 2013) focusing on two or more σ -hole interactions.

Title	Reference
Halogen, chalcogen, pnictogen and tetrel bonding	
Recognition in the Domain of Molecular Chirality: From Noncovalent Interactions to Separation of Enantiomers	Peluso & Chankvetadze (2022)
The Relevance of Experimental Charge Density Analysis in Unraveling Noncovalent Interactions in Molecular Crystals	Thomas <i>et al.</i> (2022)
A Biological Take on Halogen Bonding and Other Non-Classical Non-Covalent Interactions	Czarny <i>et al.</i> (2021)
Indirect spin–spin coupling constants across noncovalent bonds	Jaźwiński (2021)
Noncovalent bonds through σ - and π -hole located on the same molecule. Guiding principles and comparisons	Zierkiewicz <i>et al.</i> (2021)
On the Importance of σ -Hole Interactions in Crystal Structures	Frontera & Bauzá (2021)
Noncovalent Interactions at Lanthanide Complexes	Mahmudov <i>et al.</i> (2021)
Yet another perspective on hole interactions	Tarannam <i>et al.</i> (2021)
Classification of so-called non-covalent interactions based on VSEPR model	Grabowski (2021)
Electrostatics and Polarization in σ - and π -Hole Noncovalent Interactions: An Overview	Politzer & Murray (2020)
The Hydrogen Bond: A Hundred Years and Counting	Scheiner (2020)
Anion recognition based on halogen, chalcogen, pnictogen and tetrel bonding	Taylor (2020)
Unraveling the Nature of Weak Hydrogen Bonds and Intermolecular Interactions Involving Elements of Group 14–17 <i>via</i> Experimental Charge Density Analysis	Row (2020)
Unravelling the Importance of H bonds, σ -hole and π -hole-Directed Intermolecular Interactions in Nature	Pramanik & Chopra (2020)
Coordination of anions by noncovalently bonded σ -hole ligands	Scheiner <i>et al.</i> (2020)
Not Only Hydrogen Bonds: Other Noncovalent Interactions	Alkorta <i>et al.</i> (2020)
Solid-state NMR spectroscopy for the analysis of element-based non-covalent interactions	Xu <i>et al.</i> (2020)
Noncovalent interactions in metal complex catalysis	Mahmudov <i>et al.</i> (2019)
Forty years of progress in the study of the hydrogen bond	Scheiner (2019)
A Million Crystal Structures: The Whole Is Greater than the Sum of Its Parts	Taylor & Wood (2019)
The Hydrogen Bond and Beyond: Perspectives for Rotational Investigations of Non-Covalent Interactions	Juanes <i>et al.</i> (2019)
σ -Hole Interactions in Anion Recognition	Lim & Beer (2018)
Molecular electrostatic potentials and noncovalent interactions	Murray & Politzer (2017)
Non-covalent interactions in the synthesis of coordination compounds: Recent advances	Mahmudov <i>et al.</i> (2017a)
Computer Modeling of Halogen Bonds and Other σ -Hole Interactions	Kolář & Hobza (2016)
σ -Hole Bond <i>versus</i> π -Hole Bond: A Comparison Based on Halogen Bond	Wang <i>et al.</i> (2016)
The Bright Future of Unconventional σ/π -Hole Interactions	Bauzá <i>et al.</i> (2015)
σ -Hole bonding: A physical interpretation	Politzer <i>et al.</i> (2014)
Halogen and chalcogen bonding	
Halogen bonding and chalcogen bonding mediated sensing	Hein & Beer (2022)
Noncovalent interactions in proteins and nucleic acids: beyond hydrogen bonding and π -stacking	Jena <i>et al.</i> (2022)
Stereoselective Processes Based on σ -Hole Interactions	Peluso & Mamane (2022)
Frontiers in Halogen and Chalcogen-Bond Donor Organocatalysis	Bamberger <i>et al.</i> (2019)
Novel Noncovalent Interactions in Catalysis: A Focus on Halogen, Chalcogen, and Anion– π -Bonding	Breugst <i>et al.</i> (2017)
Unorthodox Interactions at Work	Zhao <i>et al.</i> (2016)
Chalcogen and pnictogen bonding	
Chalcogen and pnictogen bonds: insights and relevance	Shukla & Chopra (2021)
On the importance of pnictogen and chalcogen bonding interactions in supramolecular catalysis	Frontera & Bauza (2021)
On the Importance of σ -Hole Interactions in Crystal Structures	Frontera & Bauzá (2021)
The challenge of non-covalent interactions: Theory meets experiment for reconciling accuracy and interpretation	Puzzarini <i>et al.</i> (2020)
Halogen, chalcogen and pnictogen bonding	
Continuum in H-bond and Other Weak Interactions ($X-Z \cdots Y$): Shift in $X-Z$ Stretch from Blue Through Zero to Red	Karir & Jemmis (2020)
σ -Hole Interactions in Catalysis	Breugst & Koenig (2020)
Plane-Wave Density Functional Theory Meets Molecular Crystals: Thermal Ellipsoids and Intermolecular Interactions	Deringer <i>et al.</i> (2017)
Detailed comparison of the pnictogen bond with chalcogen, halogen, and hydrogen bonds	Scheiner (2013a)
On the reliability of pure and hybrid DFT methods for the evaluation of halogen, chalcogen, and pnictogen bonds involving anionic and neutral electron donors	Bauzá <i>et al.</i> (2013)
Halogen, pnictogen and tetrel bonding	
Hydrogen bond and other Lewis acid–Lewis base interactions as preliminary stages of chemical reactions	Grabowski (2020a)
Halogen and tetrel bonding	
The σ and π Holes. The Halogen and Tetrel Bondings: Their Nature, Importance and Chemical, Biological and Medicinal Implications	Montaña (2017)
Chalcogen, pnictogen and tetrel bonding	
Supramolecular assembly based on ‘emerging’ intermolecular interactions of particular interest to coordination chemists	Tiekink (2017)
A Survey of Supramolecular Aggregation Based on Main Group Element–Selenium Secondary Bonding Interactions – A Survey of the Crystallographic Literature	Tiekink (2020)
Pnictogen and tetrel bonding	
Pnictogen and tetrel bonds – tetrahedral Lewis acid centres	Grabowski (2019)

pyridine 1-oxide) upon formation of C—I···O halogen bonds and π -stacking interactions between the electron-rich naphthyl groups of the NPTO molecule and the electron-poor iodoperfluorobenzenes, which are interpreted in terms of a π -hole description. The crystallographic studies are complemented by quantum chemical calculations. Saha and co-workers investigate the relationship between physical properties and halogen-bond strength. Specifically, they have examined the propensity for single crystals of 4-halobenzenes to bend (Veluthaparambath *et al.*, 2022). In their article, they correlate the crystal structure of 4-iodobenzonitrile and its brittle behaviour, which contrasts with the chloro and bromo analogues that exhibit elastic bending and plastic bending, respectively. The study is supported by density functional theory (DFT) calculations and a statistical analysis of C—X···N≡C halogen-bond geometries using the CSD. Finally, Mosquera *et al.* (2023) link halogen bonding and reactivity in their study of pyridine-4-thiol (4-mercaptopyridine). Cocrystallization with the ditopic halogen-bond donor 1,4-diiodotetrafluorobenzene leads to tautomerization of the thiol to give the zwitterionic analogue with thiolate and pyridinium groups. This zwitterion employs the sulfur as the halogen-bond acceptor (C—I···S, $R_{IS} = 0.84$) in the formation of a 2:1 cocrystal (C₅H₅NS·C₆F₄I₂), in which these trimolecular supermolecules are further linked *via* N—H···S hydrogen bonds. When the cocrystallization is pursued on a larger scale, with stirring, the solution containing the two cocrystal formers leads to a nucleophilic substitution reaction that results in the chloro groups of the CH₂Cl₂ solvent being replaced by the formation of new C—S bonds to give the zwitterionic form of 4-mercaptopyridine. The resulting [CH₂(SC₄H₅N)₂]²⁺ dication crystallizes as its dichloride salt and exhibits C—S···Cl chalcogen bonds. Stabilization of the zwitterionic form of 4-mercaptopyridine in solution by halogen bonding to C₆F₄I₂ is suggested as enabling the sulfur to serve as a better nucleophile in its reaction with CH₂Cl₂.

Three articles focus on the competition or co-operation of halogen bonds with other σ -hole class (secondary bonding) interactions (Fig. 3). Pennington and co-workers report a series of 18 cocrystals between heterocyclic thiones based on benzimidazole, benzoxazole or benzothiazole with a variety of iodoperfluorobenzenes or tetraiodoethene (Watts *et al.*, 2022), leading to structures that are rich in directional intermolecular interactions. Persistent N—H···S hydrogen bonding leads to two-dimensional (2D) tape motifs or dimers depending on the number of N—H groups available. These units are then further linked by C—I···S and/or C—I···I halogen bonds and occasionally by C=S···I—C chalcogen bonds. Aakeröy and co-workers have designed a library of molecules based upon 1,3,4-chalcogenadiazoles that carry a halogen substituent at the 2-position of the five-membered ring and a 4-halophenyl group attached at the 5-position of the same ring (De Silva *et al.*, 2022). This family of molecules contains two different halogen-bond donor groups, the strengths of which differ and are tuneable, as indicated by electrostatic potential calculations of their associated σ -holes. The five-membered ring provides a chalcogen-bond donor site and acceptor sites for

both halogen and chalcogen bonds at the ring N atoms. The molecules are linked into 2D assemblies, propagated along the *c* axis by halogen bonds (C—I···I, C—Br···Br and C—Br···I) and along the *a* axis *via* bifurcated chalcogen bonds involving both ring N atoms in the acceptor role. This outcome contrasts with a prediction based simply on σ -hole electrostatic potentials, which would suggest that the strongest interaction would be halogen bonding to the ring N atom (position-3). The analysis of the interactions is supported by Hirshfeld surfaces, fingerprint plots and energy framework calculations (Spackman & Jayatilaka, 2009; Spackman *et al.*, 2021), the latter indicating that the observed chalcogen bonds make a larger electrostatic contribution to the lattice energy than the C—X···X halogen bonds. Chopra, Hathwar and co-workers report the structure of the organic salt 2,4,6-trimethylpyrylium tetrafluoroborate, C₅H₂Me₃O⁺·BF₄[−], and present an extensive computational analysis of the short intermolecular contacts to provide a description of the interaction type (Mandal *et al.*, 2022). Among the interactions indicated by the topological analysis of the calculated electron density and accompanying distributed atomic polarizability calculations are B—F···O interactions. Although not clearly described as either halogen or chalcogen bonds, NBO (natural bond orbital) analysis indicates interaction of filled F(lone pair) with O—C(π^*) orbitals. B—F···C interactions involving the *ortho*-methyl groups of the pyrylium ring and involving *ortho* ring C atoms are described as tetrel bonds.

Three articles focus solely on chalcogen bonds (Fig. 4) and reflect the growing importance and interest in this class of interactions, alongside the more extensively studied halogen bond. Huber and co-workers report the synthesis and crystal structures of a set of four 1,3-bis(benzimidazoliumyl)benzene-based compounds designed for two-point binding of suitable Lewis bases *via* chalcogen bonds (Steinke *et al.*, 2023). This class of compounds and related triazolium analogues have been used successfully as Lewis acid catalysts (with chalcogens Ch = S, Se or Te) in several benchmark reactions (Wonner *et al.*, 2017, 2019*a,b*). The crystal structures reported are of the methylimidazolium analogues of the more soluble octylimidazolium catalysts, which proved too difficult to crystallize but exhibited some unexplained trends in catalytic behaviour as a function of chalcogen choice. The current study demonstrates in most cases two-point chalcogen-bond binding of the CF₃SO₃[−] counter-ion involving one or two anion oxygen sites and exhibits single chalcogen bonds to the anion in others. These interactions are supported by other interactions, such as anion- π interactions, in some cases. The crystallographic studies are complemented by DFT calculations of molecular electrostatic potentials. White and co-workers report a study of the pyridin-3-yl derivative of the selenium-containing drug ebselen, **1** (Xu *et al.*, 2023), and its methylpyridinium iodide salt (**1**-Me⁺I[−]) and tosylate salt (**1**-Me⁺CH₃C₆H₄SO₃[−]·3H₂O). The crystal structure of the parent drug (Dupont *et al.*, 1990) and a subsequent charge-density study (Thomas *et al.*, 2015) revealed a short and strong C—Se···O=C chalcogen bond [Se···O = 2.522 (1) Å] accompanied by an IR stretching frequency shift [$\Delta\nu(\text{CO}) \simeq 71 \text{ cm}^{-1}$]. The newly reported

structures contain chalcogen bonds: C—Se···N and C—Se···O=C in **1**, C—Se···O=C in 1-Me⁺CH₃C₆H₄SO₃⁻·3H₂O and a very strong interaction that approximates the formation of an Se—I bond as a hypervalent Se. In **1**, the C—Se···N interaction is much shorter than C—Se···O=C. In each structure, the chalcogen bonding is stronger *trans* to the N—Se covalent bond than *trans* to the C—Se covalent bond and leads to a significant lengthening of this bond, consistent with charge transfer to the N—Se σ^* orbital and correlating with the strength of the chalcogen bond. An experimental charge-density study of **1** enables a more detailed analysis of the chalcogen bonding within the QTAIM (quantum theory of atoms in molecules) framework (Bader, 1991). This analysis indicates that the C—Se···N chalcogen bond exhibits significant electron sharing (albeit with a bond critical point, BCP, consistent with a closed-shell interaction), whereas the weaker C—Se···O=C chalcogen bond exhibits characteristics of a largely electrostatic interaction. Bryce and co-workers have used single-crystal and powder X-ray diffraction alongside ⁷⁷Se/¹²⁵Te magic-angle spinning solid-state NMR spectroscopy in characterizing chalcogen bonding in cocrystals of 3,4-dicyano-1,2,5-chalcogenodiazoles (Ch = Se and Te) with hydroquinone or chloride as the chalcogen-bond acceptor (Nag *et al.*, 2022). The three crystal structures reported each show chalcogen-bond formation *trans* to both N—Ch covalent bonds [N—Se···N, N—Se···O, N—Te···Cl and N—Te··· π (phenyl)]. All are relatively strong ($R_{\text{SeN}} = 0.86$, $R_{\text{SeO}} = 0.88$ and $R_{\text{TeCl}} = 0.69\text{--}0.80$; N—Ch···A = 168–175°). NMR data demonstrate the sensitivity of ¹²⁵Te chemical shift values to N—Te···A chalcogen bonds and are consistent with earlier studies of cocrystals of dicyano-1,2,5-tellurodiazole with a variety of chalcogen-bond acceptors (A) (Kumar *et al.*, 2020). The 3,4-dicyano-1,2,5-selenodiazole–hydroquinone cocrystal shows ⁷⁷Se chemical shift tensor values indicative of retention of self-complementary N—Se···N chalcogen bonds.

4. Conclusions

In this review our aim has been to summarize the current status of halogen bonds and other σ -hole interactions involving *p*-block elements in Lewis acidic roles, notably chalcogen bonds, pnictogen bonds and tetrel bonds. Our approach has been to tabulate and briefly discuss and classify review articles written mostly since 2013 that cover this topic. The present review also serves as an overview and introduction to the special issue in this journal comprising 11 articles and entitled ‘Halogen, chalcogen, pnictogen and tetrel bonds: structural chemistry and beyond,’ which presents a snapshot of some of the current research activities in the field.

5. Note (see Introduction)

The two early 19th century articles by Colin, entitled ‘*Sur Quelques Combinaisons de l’Iode*’ (Colin, 1814) and ‘*Memoire sur les Combinaisons de l’Iode avec Substances Vegetales et Animales*’ (Colin & Gaultier de Claubry, 1814), which are frequently cited as the earliest examples of halogen bonding,

are sometimes incorrectly cited in the literature. The principal author, Jean-Jacques Colin, is listed as M. Colin in the former article, but this is an abbreviation for Monsieur Colin. In the latter article, the authors are listed as MM. Colin et H. Gaultier de Claubry, but this is an abbreviation for Messieurs Colin and H. Gaultier de Claubry.

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