

Chalcogen Chemistry: Fundamentals and Applications. Edited by Vito Lippolis, Claudio Santi, Eder J. Lenardão and Antonio L. Braga. Royal Society of Chemistry, 2023. Hardcover. Pp. 728. Price EUR 156.00. ISBN 978-1-83916-422-4

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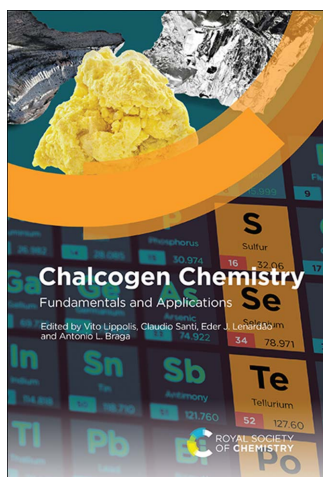
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At 728 pages, this new book on chalcogen chemistry is intended to provide an update and one-stop resource for newcomers in the chemistry of chalcogens (S, Se, Te), but also a guide to the latest results for established researchers in this field. The task is huge as chalcogen chemistry covers so many different aspects but the editors and contributors, all involved in the organization of former International Conferences on the Chemistry of Selenium and Tellurium (ICCST14/15), concentrate essentially on the organic aspects of chalcogen chemistry. As a consequence, broad topics related to inorganic and coordination chemistry such as solid-state metal chalcogenides and coordination complexes of chalcogenated ligands (chalcogenates, dichalcogenates, chalcogenoethers, ...) are only briefly mentioned. In this respect, the very general title is misleading. That being said, and with this restriction in mind, the book still efficiently covers already a very broad range of organic/molecular topics through 27 short chapters written by different contributors. It is organized into six areas: (i) a few selected examples of recent coordination chemistry of chalcogenated molecules (Chapters 1 to 4), (ii) main-group derivatives and chalcogenated heterocycles (Chapters 5 to 7), (iii) chalcogen-based reagents in organic chemistry (Chapters 8 to 13), (iv) physical chemistry approaches (fluorescence modulation, ^{77}Se NMR) in Chapters 14 and 15, (v) chalcogen bonding and its applications in structural and supramolecular chemistry (chapters 16 to 19), and (vi) the biological role, and therapeutic and nutrition applications of chalcogenated molecules (Chapters 21 to 27).

Chapter 1 (Shieh & Li) deals with a few examples of metal carbonyl chalcogenide clusters, eventually associated into extended structures, with interesting magnetic properties as two electron-precise $\text{Te-Mn} [\text{Mn}_6\text{Te}_n(\text{CO})_{18}]^{4-}$ ($n = 6, 10$) anionic complexes. Chapter 2 (Mutoh) describes recent achievements in the chemistry of CS, CSe and CTe analogs of the carbonyl (CO) ligand in coordination chemistry, with an extension to the analogs of nitrosyl, *i.e.* NS and NSe, providing a really useful and comprehensive collection of spectroscopic and selected X-ray data on this attractive chemistry. Chapter 3 (Jain & Chauhan) concentrates on the metal chalcogenolates used as single source molecular precursors of metal chalcogenide nanocrystals and thin films, *i.e.* those bringing steric constraints (*tert*-butyl and trimethylsilyl). The versatility of such systems also allows for the elaboration of ternary and quaternary chalcogenide semiconductors for photovoltaic and thermoelectric devices. In Chapter 4 (by Pop, Silvestru & Silvestru), so-called pincer ligands are introduced, based on a phenyl or pyridine moiety substituted in 2- and 6-positions with $\text{C}=\text{E}$ or $\text{P}=\text{E}$ groups ($\text{E} = \text{S, Se, Te}$). The authors concentrated on the most recently reported coordination complexes, considering the already large number of reviews on these series, however, essentially investigated only with sulfur.

In Chapter 5 (Puylaert, Beckman & Hupf), we move from coordination chemistry to main group derivatives of chalcogens. Heterocycles combining group 13 (B, Al, Ga), group 14 (Si, Ge, Sn) or group 15 (P, As, Sb) elements with chalcogens are described together with their reactivity, revealing a rich diversity of four-membered, five-membered systems as well as cage compounds. The Woollins reagent $(\text{PhPSe}_2)_2$ is introduced here



for the first time as an example of a four-membered P_2Se_2 ring and many examples involving tellurium are reported here. Reactivity studies are developed first in Chapter 6 (Penteado & Alberto) on nitrogen-based heterocyclic compounds, involving electrophilic chalcogen reagents, together with interesting photo- or electrochemical activation processes. Chapter 7 (Zibarev) follows with chalcogen-containing heterocycles, specifically here the neutral radicals 1,2,3- and 1,3,2-benzodichalcogenazolyls and anionic analogs and their interesting magnetic properties, enhanced in the few reported selenium derivatives. I only regret that the active field of organic conductors and superconductors, single-component conductors based on chalcogenated molecules (tetrathiafulvalenes, chalcogeno-arenes, dithiolene complexes) has not been included here in an extra chapter.

From Chapter 8 to Chapter 13, we enter the world of chalcogen-based reagents in organic chemistry. Chapter 8 (Maekawa & Murai) concentrates on phosphine selenides, including the Woollins reagent of course but also chiral derivatives used as Lewis base catalyst toward asymmetric sulfenylation. Chirality at the sulfur atom is the core topic of Chapter 9 (Krasowska *et al.*), with a clear presentation of the different families, and the latest results on this topic where recent reviews are abounding. Chiral Se- and Te-containing derivatives based on chiral pool functionalization are illustrated in Chapter 10 (Scianowski *et al.*) for enantioselective reagents as nucleophiles, electrophiles, and catalysts, several topics which will be developed in the forthcoming chapters in their achiral version. Indeed Chapter 11 (Rafique, Azeredo & Saba) reports on the most used electrophilic reagents (diselenides, selenium halides, *N*-chalcogenoamides) for the formation of carbon–chalcogen bonds while Chapter 12 (Tanini, Capperucci & Menichetti) focuses on ‘unconventional’ nucleophilic S and Se reagents containing chalcogens bonded to boron, aluminium, silicon and tin, providing very useful alternatives to the classical thiolate and selenolate nucleophiles. Chapter 13 (Back) closes the synthetic chemistry part of this book by concentrating on the role of selenated compounds as catalysts, essentially in the oxidative addition/cyclization of alkenes and the oxidation of alcohols and amines.

Organochalcogen-based fluorescent sensors described in Chapter 14 (Dos Santos, Manjare *et al.*) are based on a modulation of the emission properties of a fluorophore (such as BODIPY) linked to a Se/Te moiety upon reaction with reactive oxygen (nitrogen) species ROS (RNS). The interest of ^{77}Se NMR with its wide chemical shift range (> 6000 p.p.m.), is shortly illustrated in Chapter 15 (Santos Silva and Orian) with an opening to the most recent computational approaches.

In Chapters 16 to 19, the recent results on the so-called chalcogen bonding and its applications in structural and supramolecular chemistry, organic synthesis/catalysis, and crystal engineering are developed. In Chapter 16, Aragoni and Torubaev present an original and systematic study on the structural features of the linear fragments $R-Ch \cdots Nu$ ($Ch = S, Te$; $R-Ch \cdots Nu$ angle in the range 160 – 180°) found in the Cambridge Structural Database (Groom *et al.*, 2016).

Computational methods to investigate ChB are briefly reviewed in Chapter 17 (Arca, Ciancaleoni & Pintus) while the emerging role of ChB as a useful tool in anion recognition effects and in crystal engineering is nicely illustrated in Chapter 18 (Vargas-Baca & Bonifazi). The Lewis-acidic character of such chalcogen bond donors (cationic *versus* neutral, mono *versus* bidentate) is currently being exploited in organocatalysis, as illustrated in Chapter 19 (Huber). Chapter 20 (Laitinen) closes this section by concentrating on the syntheses and structures of macrocyclic seleno- and telluroethers, with porous, columnar structures appearing with the largest cyclic telluroethers stabilized by $Te \cdots Te$ intermolecular interactions.

The seven following short chapters (Chapters 21 to 27) of his book concentrate on the biological role, and therapeutic and nutrition applications of chalcogenated (essentially selenated) molecules, amino acids and nucleic acids. In Chapter 21 (Da Rocha), the Ebselen molecule is presented, with a detailed report on its history, starting from its synthesis back in 1924, 99 years ago, to the different clinical trials taking advantage of its antioxidant effects. Chapter 22 (Sancineto & Nascimento) explores the therapeutic role of ebselen and its analogs, together with diselenides, for their antiviral activity (as recently explored with SARS-Cov-2) and neurodegenerative diseases. Chapter 23 (Flohé) provides a very interesting overview of the history of glutathione peroxidases (GPx) and its co-substrate (GSH), highlighting the role of selenocysteine as the catalytic site for reaction with peroxides. In Chapter 24 (Iwaoka), the syntheses and applications of chalcogen-containing proteins and nucleic acids is discussed on the basis of the most recent results such as, in proteins, the replacement of S–S bridges by Se–Se ones, or the reactivity of S–Se bridges. This oxidative folding of cysteine-containing proteins can be harmed in the presence of ROS or RNS (see Chapter 14) and small selenium-containing molecules (ebselen, selenides and diselenides) used as peroxidase mimics are presented in Chapter 25 (Arai). The methods used for quantification of selenium content in food and environment are exposed in Chapter 26 (Pacheco), highlighting the important role of LC-ICP MS techniques. In Chapter 27, Tommasini stresses the role of dietary sources of S and Se to reach the healthy levels in the human body (140 g S in a 70 kg reference male), illustrating the adverse outcomes of both deficiency and excess of Se in humans.

Altogether the book is easy to read and presents an appreciable homogeneity and quality in the writing and the illustrations. In all chapters, the authors give references to the most important and recent full reviews on their respective topics and concentrate in their contributions on the latest results published in the last 10 years, providing a very useful tool to enter each topic. This book will be therefore quite of interest to younger colleagues entering the field, giving them a broad overview of the organic and molecular chalcogen chemistry, with references to many recent, more detailed reviews. Beyond the crystallographically characterized derivatives found in many chapters, the interest for *Acta Crystallographica* readers is perhaps more limited to the Chapters 16–

19 introducing chalcogen bonding (see also Brammer *et al.*, 2023; Shukla *et al.*, 2020). From my perspective, I consider that the reading of this thick volume is worth the effort, as I discovered in more detail and with useful references to many aspects of chalcogen chemistry I was aware of only superficially. Such a book provides the opportunity to link together many different aspects of the rich chemistry of chalcogens.

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