Handbook of Chalcogen Chemistry
New Perspectives in Sulfur, Selenium and Tellurium
To my delightful grandchildren
Francesco and Silvia
Handbook of Chalcogen Chemistry
New Perspectives in Sulfur, Selenium and Tellurium

Edited by

Francesco A. Devillanova
Department of Inorganic and Analytical Chemistry, University of Cagliari, Italy
Preface

Up to a few decades ago, chalcogen chemistry was centred almost exclusively on sulfur, selenium being marginal compared to it and the chemistry of tellurium being practically inexistent. For many years the chemistry of Se and Te has grown rapidly: this is easily seen with an electronic search on SCIfinder comparing 1941–1950 and 1991–2000 and using as entries “sulfur/selenium/tellurium compounds”. The percentage of papers on Se/Te rises from 13.4% (on a total 335 papers) for the former period to 27.7% (on a total 1905 papers) for the latter. A number of factors have contributed to this increase in the interest in the chemistry of Se and Te. One is the development of new suitable synthetic methodologies that avoid the use of obnoxious reagents (CSe₂, H₂Se, etc.), but most importantly the great variety of technological applications that can be found for their many compounds. To this purpose I would like to recall that compounds from the class of the charge-transfer salts of chalcogen-rich molecules, such as tetrathiafulvalene (TTF), or from that of 1,2-dichalcogenolenes, or the variegated area of metal chalcogenides are extremely important in Materials Science for their potential applications, which span from n-dimensional molecular conductors to magnets, to bistable switchable materials, and to NLO materials, to quote only a few. Further examples of this increasing trend, which is always of great topical interest, are the fundamental research works in the field of coordination chemistry with a large variety of ligands containing chalcogen atoms for the preparation of new precursors for metal–chalcogenide vapour deposition, of metalloenzymes containing multimetallic centres as active sites for a number of catalytic reactions, or of chalcogen-containing mixed macrocycles with signalling functional groups as sensors for heavy metal-ion recognition, and so forth.

The simplest way of organizing a handbook that contained an incredible amount of results from research on chalcogen chemistry while avoiding to omit important topics appeared to me that of considering the chemistry of chalcogen elements in combination with all other elements of the periodic table. On the other hand, an ambitious purpose of the book was to point out the increasing role of chalcogen elements in multidisciplinary fields such as biochemistry and materials science. For these reasons, the Handbook of Chalcogen (S, Se, Te) Chemistry was structured on a multidisciplinary approach by putting together contributions ranging from organic to inorganic and analytical chemistry, synthetic to structural and theoretical chemistry, biological to material and supramolecular chemistry. It was then divided into two parts: in the first of
these the chapters are identified by the elements that are bonded to the chalcogen atoms, from boron to the halogens, including the chalcogens themselves. The overview ends with two chapters on metal–chalcogenides and metal–polychalcogenides. The second part of the book includes peculiar aspects of chalcogen chemistry that represent attractive fields of research in biological, materials and supramolecular chemistry, as well as a few miscellaneous chapters on particular topics. When different leitmotifs are considered in organizing the same subject matter, one still runs the risk of overlaps among the different chapters even though great care is devoted to avoid this negative aspect. There is one positive aspect, however, which outbalances the negative one: i.e., the two parts are strictly interrelated, since the chapters in the second part are further developments of those in the first part. Thus, the chapter on the chalcogen–nitrogen bond (Chapter 4) has its counterpart in the one on stable radicals (Chapter 12.1), where it is clearly shown that fundamental research on chalcogen–nitrogen compounds can open unthinkable perspectives for the use of organic radicals in building magnetic materials. Similarly, the chapters on the chalcogenolate (Chapter 2.1) and 1,1-dichalcogenate (Chapter 10.2) ligands show that their coordination chemistry is always topical and widely exploited for potential applications in many different fields, such as that of preparing enzyme mimetic models (Chapter 11.2). The chapters on chalcogen-rich donors (Chapter 12.2) and on dithiolenes (Chapter 12.3) can be considered a continuation of those on chalcogen–carbon compounds: many compounds of both classes have found a large number of technological applications thanks to their conducting, magnetic, and optical properties. For this reason, both classes of compounds have strongly contributed to the increasing interest in chalcogen chemistry. In the same way, some important technological applications that have been found for a number of metal chalcogenides (Chapter 9.1) and polychalcogenides (Chapter 9.2) together with their remarkable diversity in their structure and properties have been the driving force of the incredible expansion of these areas of research. The ability of chalcogen elements to catenate is responsible for the great variety of molecular forms of chalcogen elements, of their cations (Chapter 7.1) and anions (Chapter 9.2), of their organic di- and poly-chalcogenides, and of their organic multication species (Chapter 7.2). Finally, the chalcogen-halogen compounds, both binary (Chapter 8.1) and those that derive from reactions of a variety of chalcogen-containing donors with halogens/interhalogens (Chapter 8.2), which are extensively dealt with in the first part of the book, appear consistently in the second part, as they provide interesting examples of hypervalency of the chalcogen elements (Chapter 10.3) and represent attractive examples of supramolecular structures (Chapter 13) built thanks to the ability of chalcogen-halogen bonds to give directional secondary bonds, in competition with other interactions (hydrogen bonding, dipole-dipole interactions, etc.). Though not exhaustive, the book includes mainly the results of the last decade and illustrates the tendencies of the most appealing research work. Particular attention has been paid by the authors to update the literature almost up to the end of 2005.
The book is a candidate to become a reference book for future years. The multidisciplinary approach, with chapters reserved to biological, materials, and supramolecular chemistry, presents the book as an important source of information not only for chemists but also for physicists, biochemists, and other researchers, who in some way deal with chalcogen compounds. I hope the book may induce some curiosity in the reader and attract him towards this kind of chemistry.

I am greatly indebted to all authors for their commitment and to my collaborators for useful discussions.
## Contents

### Chapter 1 Compounds Containing the Boron–Chalcogen B–E (E= S, Se, Te) Bond

*Michael A. Beckett*

- 1.1 Introduction 1
- 1.2 Books and Review Articles 1
- 1.3 Polyhedral Boron Hydride Derivatives 2
  - 1.3.1 Species with Exo B–Chalcogen Bonds 2
  - 1.3.2 Species with Chalcogen Atoms within the Cage 8
- 1.4 Binary, Ternary, and Quaternary Chalcogenoborates 14
- 1.5 Heterocycles Containing B–E Linkages 17
- 1.6 Miscellaneous Boron-Chalcogen Compounds and Reagents 19
- Abbreviations 22
- References 22

### Chapter 2.1 Thiolates, Selenolates, and Tellurolates

*M. Concepción Gimeno*

- 2.1.1 Introduction 33
- 2.1.2 Synthetic Routes of Ligands and Metal Chalcogenolates 34
  - 2.1.2.1 Synthesis of the Chalcogenols 34
  - 2.1.2.2 Synthesis of Metal Chalcogenolates 34
- 2.1.3 Alkali and Alkaline Earth Derivatives 36
- 2.1.4 Main Group Metal Derivatives 39
  - 2.1.4.1 Zinc, Cadmium, and Mercury 39
  - 2.1.4.2 Aluminium, Gallium, Indium, and Thallium 41
  - 2.1.4.3 Antimony and Bismuth 42
  - 2.1.4.4 Germanium, Tin, and Lead 43
Chapter 2.4  Thioamides, Thioureas and Related Selenium and Tellurium Compounds

Mamoru Koketsu and Hideharu Ishihara

2.4.1 Introduction 145
2.4.2 Thioamides 145
  2.4.2.1 Synthesis of Thioamides 146
  2.4.2.2 Heterocycles Using Thioamides 151
  2.4.2.3 Transformation of Thioamides 156
  2.4.2.4 Calculations 160
  2.4.2.5 Biological Activities 160
2.4.3 Thioureas 160
  2.4.3.1 Synthesis of Thioureas 160
  2.4.3.2 Heterocycles Using Thioureas 165
  2.4.3.3 Transformation of Thioureas 169
  2.4.3.4 Application as Sensor 171
  2.4.3.5 Application as Ligand 172
  2.4.3.6 Glycosyl Thioureas 172
  2.4.3.7 Biological Activities 172
2.4.4 Cyclic Chalcogenoureas 173
2.4.5 Selenoamides and Selenoureas 177
  2.4.5.1 Synthesis of Selenoamides and Selenoureas 178
  2.4.5.2 Heterocycles Using Selenoamides and Selenoureas 180
2.4.6 Telluroamides and Telluroreusas 181
References 182

Chapter 3  The Compounds Between Si, Ge and Sn and Chalcogens (S, Se, and Te) Having Both a Single Bond and a Double Bond (Heavy Ketones)

Nobuhiro Takeda, Norihiro Tokitoh and Renji Okazaki

3.1 Introduction 195
3.2 The Compounds Having a Single Bond between Si, Ge, and Sn and Chalcogens 195
  3.2.1 Structural and Spectroscopic Properties 196
  3.2.2 Formation of Single Bonds between Heavier Group 14 and 16 Elements 196
  3.2.3 Reactions 202
3.3 The Compounds Having a Double Bond between Si, Ge, and Sn and Chalcogens (Heavy Ketones) 207
  3.3.1 Theoretical Aspects 207
  3.3.2 Structural and Spectroscopic Properties 208
  3.3.3 Syntheses 211
  3.3.4 Reactivities 211
References 215
4.1 Introduction

4.2 General Considerations

4.3 Characterization of Chalcogen-Nitrogen Compounds

4.3.1 Diffraction Techniques

4.3.2 $^{14}$N and $^{15}$N NMR Spectroscopy

4.3.3 $^{33}$S, $^{77}$Se and $^{125}$Te NMR Spectroscopy

4.3.4 ESR Spectroscopy

4.3.5 Infrared and Raman Spectroscopy

4.4 Binary Chalcogen-Nitrogen Systems

4.4.1 Neutral Molecules

4.4.2 Cations

4.4.3 Anions

4.5 Metal Complexes of Binary Chalcogen-Nitrogen Ligands

4.5.1 Thionitrosyl and Selenonitrosyl Complexes

4.5.2 Cyclometallathiazenes

4.6 Chalcogen-Nitrogen Halides

4.6.1 Thiazyl Halides NSX (X = F, Cl, Br) and the [NSX$_2$]$^-$ Anions (X = F, Cl)

4.6.2 Thiazyl Trifluoride, NSF$_3$, and Haloimino-sulfur Difluorides, XNSF$_2$ (X = F, Cl)

4.6.3 Acyclic Chalcogen-Nitrogen-Halogen Cations [N(ECl)$_2$]$^+$ (E = S, Se) and [N(SeCl)$_2$]$_2^-$

4.6.4 Tellurium-Nitrogen-Chlorides [Te$_4$N$_2$Cl$_8$]$^{2+}$ and Te$_{11}$N$_6$Cl$_{26}$

4.6.5 Thiodithiazyl and Selenadiselenazyl Dichloride [E$_3$N$_2$Cl]Cl (E = S, Se)

4.6.6 Cyclotrithiazyl Halides (NSX)$_3$ (X = Cl, F)

4.6.7 Dihalocyclotetraethiazenes S$_4$N$_4$X$_2$ (X = Cl, F) and Cyclotetrahthiazyl Fluoride (NSF)$_4$

4.6.8 Sulfanuric Halides [NS(O)X]$_2$ (X = Cl, F)

4.7 Chalcogen-Nitrogen Oxides

4.7.1 The Thionyl Imide Anion, [NSO]$^-$

4.7.2 The Thionitrite and Perthionitrite Anions, [SNO]$^-$ and [SSNO]$^-$

4.7.3 The [SO$_x$N$_3$]$^-$ (x = 2, 3) Anions

4.7.4 $^{2}$His(Sulfinylamino)Chalcogenanes E(NSO)$_2$ (E = S, Se, Te)

4.7.5 Cyclic Chalcogen–Nitrogen Oxides

4.8 Acyclic Organic Chalcogen-Nitrogen Compounds

4.8.1 Chalcogenonitrosyls, RNE (E = S, Se)
4.8.2 Organic Chalcogenylamines RNEO (E = S, Se, Te) 244
4.8.3 N-Thiosulfinylamines, RNSS 245
4.8.4 Chalcogen Diimides RN=E=NR (E = S, Se, Te) 246
4.8.5 Imido Chalcogen Halides 248
4.8.6 Triimidochalcogenites, [E(NR)3]2− (E = S, Se, Te), and Sulfur Trimides, S(NR)3 249
4.8.7 Tetraimidosulfate, [S(N^tBu)4]2−, and Methyleneimidosulfate, [H2CS(N^tBu)3]2− 250
4.8.8 Chalcogen Diamides Ex(NR2)2, (E=S, Se, Te; x=1-4) 250
4.8.9 Organochalcogenyl Azides and Nitrenes 251
4.8.10 S-Nitrosothiols RSNO 252
4.8.11 Trisulfenamides, (RS)3N, and the Radical [(PhS)2N]* 252

4.9 Cyclic Chalcogen Imides 253
4.9.1 Cyclic Sulfur Imides 253
4.9.2 Cyclic Selenium and Tellurium Imides 254

4.10 Carbon-Nitrogen-Chalcogen Ring Systems 255
4.10.1 Five-Membered Rings 255
4.10.2 Six-Membered Rings 258
4.10.3 Seven-Membered Rings 260
4.10.4 Eight-Membered Rings 261
4.10.5 Bicyclic Ring Systems, RCNS3 262

4.11 Chalcogen-Nitrogen-Phosphorus Ring Systems 263
4.11.1 Chalcogen-Nitrogen-Phosphorus(V) Rings 263
4.11.2 Chalcogen-Nitrogen Rings Containing Phosphorus(III) or Other p-Block Elements 267

4.12 Chains and Polymers 267
4.12.1 Poly(Sulfur Nitride), (SN)x, and Related Polymers 267
4.12.2 Sulfur-Nitrogen Chains 269
4.12.3 Sulfur-Nitrogen Polymers Containing Three-Coordinate Sulfur(IV) 270
4.12.4 Sulfur-Nitrogen Polymers Containing Four-Coordinate Sulfur(VI) 270

4.13 Outlook 272
References 272

Chapter 5 Chalcogen–Phosphorus (and Heavier Congeners) Chemistry 286
Rob Davies

5.1 Introduction 286
5.2 Preparation, Characterisation and Properties of Compounds Containing Phosphorus-Chalcogen Bonds 288
5.2.1 Phosphorus Chalcogenides \([P_nE_m]\) and Chalcogeno-Phosphate Anions \([P_nE_m]^{x-}\)  288
5.2.2 Tertiary Phosphine Chalcogenides \([R_3PE]\)  291
5.2.3 Diphosphine Di- and Mono-Chalcogenides \([R_2P(E)-R'P(E)R_2 \text{ and } R_2P(E)-R'PR_2]\)  293
5.2.4 Secondary Phosphine Chalcogenides \([R_2P(E)H]\)  295
5.2.5 Dichalcogenophosphinic Acids \((R_2PE_2H)\) and their Derivatives  297
5.2.6 Trichalcogenophosphonic Acids \((RPE_3H_2)\) and their Derivatives  300
5.2.7 Amido and Imido Derivatives of Chalcogeno-Phosphorus Acids  302
5.2.8 Dichalcogenoimidodiphosphinates \([R_2P(E)NHP(E)R_2]\)  307
5.2.9 Phosphorus-Chalcogen Containing Heterocycles  309

5.3 Coordination Chemistry of Ligands Containing Phosphorus-Chalcogen Bonds  312
5.3.1 Phosphorus Chalcogenides \((P_nE_m)\) and Chalcogeno-Phosphate Anions \((P_nE_m)^{x-}\)  312
5.3.2 Tertiary Phosphine Chalcogenides \((R_3P = E)\)  314
5.3.3 Diphosphine Di- and Mono-Chalcogenides \([R_2P(E)-R'P(E)R_2 \text{ and } R_2P(E)-R'PR_2]\)  315
5.3.4 Secondary Phosphine Chalcogenides \((R_2PEH)\)  317
5.3.5 Dichalcogenophosphinic Acids \((R_2PE_2H)\) and their Derivatives  318
5.3.6 Trichalcogenophosphonic Acids \((RPE_3H_2)\) and their Derivatives  322
5.3.7 Amido and Imido Derivatives of Chalcogeno-Phosphorus Acids  323
5.3.8 Dichalcogenoimidodiphosphinates \([R_2P(E)NHP(E)R_2]\)  326

5.4 Applications of Compounds and Complexes Containing Phosphorus-Chalcogen Bonds  327
5.4.1 Reactions with Organic Substrates  327
5.4.2 Pesticides and Nerve Agents  330
5.4.3 Precursors Towards Metal Chalcogenide Thin-Films and Quantum Dots  331
5.4.4 Metal Extraction Technologies  334
5.4.5 Lubricant Additives  334
5.4.6 Other Applications  335

References  335