

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 (CSe_2 , H_2Se , *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.

