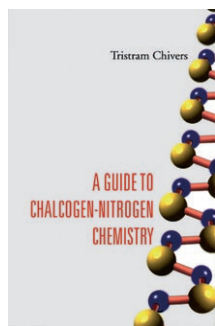


A Guide to Chalcogen–Nitrogen Chemistry



By Tristram Chivers.
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In 1835, ten years after the discovery of benzene, Gregory was the first to detect S_4N_4 , which is one of the most fascinating of all chalcogen–nitrogen compounds. That historical event serves as the introduction to this book on the molecular chemistry of chalcogen–nitrogen compounds. The author, who for several decades has been one of the leading scientists in this field, begins by explaining, in short clear sentences, why he has written the book. One might think that the molecular chemistry of chalcogens is a very old area of chemistry, and in every good textbook of inorganic chemistry one will find something about the explosive compound S_4N_4 or the polymer $(SN)_x$. But is that everything? What about the heavy homologues? This is a field that has made enormous advances, particularly in the last ten years. One finds that even less has been written in standard textbooks about reaction mechanisms and the properties and (potential) applications of chalcogen–nitrogen compounds. It is true that there are many review articles, which are listed at the end of the first chapter of this book, but so far there has been no work devoted to the subject as a whole and its basic concepts, ranging from molecules to polymers, from synthesis to reaction mechanisms, and from properties to applications. In this book the author has cleverly filled a gap with his highly informative presentation concentrating on the essentials of the subject, while not forgetting to provide a wealth of references to the original literature (up to the middle of 2004) at the end of every chapter. Therefore, the book can be recommended both as a reference source for

scientists and university teachers and as a textbook for advanced students who wish to obtain a deeper knowledge of chalcogen–nitrogen chemistry. However, it is also very suitable for everyone who can enjoy reading about an exciting area of molecular chemistry.

In the introduction, the author starts from considerations about electronegativity and the rules of double bonds, and leads the reader on to short sections about the different classes of compounds, which are then discussed in detail in the following text. As the author is dealing only with chalcogen–nitrogen compounds in which the number of heteroatoms is greater than the number of carbon atoms (excluding carbon atoms that are part of a substituent), he also soon makes it clear that this is not an encyclopedic work. The approach to the subject is interesting from a teaching standpoint, and has probably originated from a series of lectures. The introduction is followed by a short chapter about synthesis and how chalcogen–nitrogen compounds can be formed, then by a lucid description of the analytical methods that can be used for detection and characterization (X-ray, IR, Raman, NMR, EPR, and PES methods are described, with examples). That is followed by a detailed description of electronic structure and reactivity, in which simple concepts that are mostly already familiar from classical organic chemistry (Hückel aromaticity, frontier orbital theory, etc.) are applied to chalcogen–nitrogen chemistry. Simple black-and-white graphics are included so that the concepts can be quickly grasped. Building on the description of the bonding situation (often with reference to DFT-MO calculations), the author discusses the different reaction mechanisms involved in this chemistry, and the reactive properties of chalcogen–nitrogen compounds. However, what I feel this chapter lacks is an introduction to the valence-bond (VB) description of many of the structures in the figures, and some reference to the problem of hypervalent compounds, in particular when discussing electron-rich EN species ($E = \text{chalcogen}$).

It is not until the fifth chapter that the author begins a highly structured description of the chemistry of chalcogen–nitrogen compounds, in which he frequently refers back to the concepts

explained in the preceding four chapters. Here the reader can apply the knowledge that has been gained from Chapters 1–4. As expected, the description begins with the chemistry of binary systems (neutral, anionic, and cationic molecules, and species in the form of chains, rings, and cages). That is followed by a description of cyclic chalcogen imides and metal complexes, which then leads on to chalcogen–nitrogen–halogen and chalcogen–nitrogen–oxygen compounds. Each chapter again begins with a short introduction to the compound class, which gives the chapter a self-contained quality. One of the following chapters, which deal with carbon–nitrogen–chalcogen compounds, is of particular interest, namely Chapter 11 on cyclic carbon–nitrogen–chalcogen compounds. There the reader learns about where chalcogen–nitrogen chemistry might lead in the future, with possibilities ranging from monomeric free radicals to polymers, which, in conjunction with specific properties (magnetism, electrical conductivity) could serve as functional materials. The same also applies to the chapter on chalcogen–nitrogen chains and polymers, which is followed by an instructive and well-written chapter on heterocyclothiazenes and heterocycloselenazenes. The latter can serve as important precursors: for example, they can undergo thermal ring-opening polymerization to give inorganic polymers. The book ends with a short chapter on weak intramolecular chalcogen–nitrogen interactions, which are often of crucial importance for explaining the reactive properties, and can confer stability on reactive functional groups.

The author has succeeded in giving a comprehensive, stimulating, and didactically skillful treatment of chalcogen–nitrogen chemistry in a very handy book. The short chapters are systematically constructed and complement each other well in their contents, as can be seen from a quick look at the list of contents. The book is easy to read and will give readers an enthusiasm for molecular chemistry.

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