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Book review

The Chemistry of Organic Germanium, Tin and Lead Compounds

Saul Patai (ed)
Wiley, Chichester, 1995
xv + 997 pages. £280
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Saul Patai follows the excellent principle of excluding from treatment any topic that is easily available in other reviews or textbooks. The Contents page reminds you of the menu in an upmarket restaurant: few of the familiar 'meat and two veg.' items, and more of those of the less-familiar, thought-provoking kind.

The present volume is no exception. It contains 19 chapters on topics which, in the main, have not been adequately reviewed in recent years. A special advantage is that most chapters do not treat each of the three metals separately, but give a comparative treatment which is particularly useful. The literature is covered up to the end of 1994. Chapters on mass spectra, NMR and Mössbauer spectroscopy, organo-germanium, -tin and -lead compounds as synthons, analogues of carbenes and carbon radicals, rearrangements, and biochemistry have been held over to a subsequent volume.

The first chapter (96 pages), by H. Basch and T. Hoz, deals with the nature of the carbon–metal (Ge, Sn, Pb) bond. *Ab initio* methods are used to determine the geometries of a generic set of MH_3Y molecules (where M is a Group 14 element, including C and Si) and Y is one of a large range of substituents. There are extensive tables of bond lengths, Mulliken populations, charges (at the MP2 level), the derived group charges for H_3M and Y, the individual contributions of the *s*, *p* and *d* orbitals, dipole moments, molecular energies and bond dissociation energies. These data are then discussed against the experimental results which are available. This is a chapter largely for the theorist, but will be useful to the experimentalist who wants to interpret in detail his results.

Chapter 2 gives an overview by K. M. Mackay of the structures of organo-germanes, -stannanes and -plumbanes, both bivalent and tetravalent, which have been determined by diffraction methods (hence structures in solution are not covered). I am not aware of any recent review which integrates the information available on the three metals. This is an extensive and rapidly expanding field, and by a judicious selection of material it has been reduced to a manageable size (98 pages).

Stereochemistry and conformation is considered by J. A. Marshall and J. A. Jablonowski, and deals particularly with compounds with the chirality centred on the metal atom, and with compounds R^*MR_3, where the chirality is centred in the ligand R*. Much of the interest in these compounds of course lies in their use in investigating their reaction mechanisms, and it is very useful to have an up-to-date review of the field.

Chapter 4, by Simões, Liebman and Slayden, reviews the thermochemistry of organometallic compounds of germanium, tin and lead. It is a comment on the paucity of work in this field that bond dissociation enthalpies are given for only Ge–H, Ge–R, Ge–Ge, Sn–H, Sn–R, Sn–Sn and Pb–R bonds, and that the whole topic can be covered in 22 pages. Neumann's clear-cut work on the reversible dissociation of hexa-aryldistannanes could have been included. The present interest in synthetic methods involving radical reactions of silanes, germanes and stannanes would be helped if many more bond dissociation enthalpies were available.

The ESR spectroscopy of the organometallic radicals is reviewed by J. Iley. There have been few developments in this field in recent years, but it is valuable to have a thorough comparison between the three metals.

Photoelectron spectroscopy is covered by C. Cauletti and S. Stranges. The sequence of peaks in the spectrum reflects the sequence of unoccupied molecular orbitals, and the intensities of the bands reflect the electron population of the level (i.e. the orbital degeneracy) and the energy of the ionizing radiation coupled with the symmetries of the orbitals. The technique thus can give evidence of phenomena such as electronic configuration, substituent effects, C–M hyperconjugation and p_π–d_π interaction.

Chapters 7, 8 and 9, all by J. Zabicky and S. Grinberg, cover analytical aspects of organic compounds of germanium, tin and lead respectively. All aspects of analysis are included — elemental analysis principally by wet ashing or combustion, trace analysis methods such as atomic absorption or emission, spectrophotometric methods, electrochemical methods, nuclear activation, derivatization procedures, methods allowing speciation often involving chromatography coupled with a technique such as mass spectroscopy, and methods of structural analysis such as IR, Raman and NMR spectroscopy and X-ray crystallography. The underlying significance of much of this work is of course the problem of monitoring environmental pollution by organotin and, particularly, organolead compounds.

Chapter 10, by J. M. Tsangaris, R. Willem and M. Gielen, deals with the synthesis of the organometallic compounds, though the three metals here are treated separately. Methods of forming the M–C, M–H and M–halide bonds are covered.

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The next chapter, by A. Schulz and T. A. Klapötke, deals with experimental and computational results regarding the acidity, complexing, basicity and H-bonding of germanium, tin and lead compounds. In this context H-bonding refers to the M–H bond, and not the bridging potential of hydrogen, and these hydrides are considered as a separate topic with little reference to complexing or basicity. The metals in the oxidation states II and IV are discussed separately, and a number of organic-free examples are included. The section on theory gives a useful survey of the application of *ab initio* calculations to compounds of the heavier metals, and particularly to π-bonding in Group 14, to the ethane analogues $H_3M{-}M'H_3$, and the cyclotri-germanes and -stannanes, $(H_2M)_3$.

M. Charton considers substituent effects of germanium, tin and lead groups. Structure–properties quantitative relationships are used to derive various electrical and steric substituent constants and intermolecular force parameters, and then these constants are applied to various aspects of chemical reactivity and chemical and physical properties.

Chapter 13, by M. Michman, provides a thorough review of the electrochemistry of the compounds. This has a declining importance in the synthesis of organolead compounds, but an increasing importance in analysis, particularly for on-line continuous monitoring.

Chapter 14, by C. M. Gordon and C. Long, deals with the photochemistry of the organic derivatives of germanium, tin and lead. This involves mainly the formation and reactions of $R_3Sn^{\bullet}$ and R_2Sn: species, and a miscellany of pericyclic reactions. Little use has been made as yet of this chemistry in synthesis, but it can be important in the environmental degradation of the organometallic compounds.

K. C. Westaway and H. Joly describe the synthesis and uses of organic derivatives or germanium, tin and lead isotopically labelled at the metal, or in a ligand, principally with ^2H or ^{13}C. Most of these compounds have been prepared for studies of structure and of reaction mechanism, though some have been used in environmental and metabolic studies. Also included are the use of labelled organometallic compounds (e.g. Bu_3SnD) for preparing labelled non-metallic compounds, and the application of organotin compounds for preparing radioactive halides for use as radiopharmaceuticals.

Chapter 16, by P. J. Craig and J. Y. van Elteren, deals with environmental methylation of germanium, tin and lead by organisms present in river, estuarine and marine sediments. It is suggested that tin can be added to arsenic and mercury, for which methylation has been established, but the case for germanium and lead is not yet proven.

Chapters 17 and 18 give short accounts of the toxicity of organogermanium (E. Lukevics and L. M. Ignatovich) and organotin (L. R. Sherman) compounds, and the final chapter, by S. Maeda, deals with safety and environmental aspects of compounds of the three metals. There is some overlap between the coverage in this last chapter and the three previous ones.

Any group that is working on the chemistry of these families of compounds will want to have access to this volume in the library.

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