Homopolyatomic Anions. The Synthesis and Characterization of the Novel Paramagnetic Nonastannide(3−) Anion Sn_9^{3-}, a D_{3h} Cluster with 21 Skeletal Electrons

Susan C. Critchlow and John D. Corbett*

Ames Laboratory[1] and Department of Chemistry
Iowa State University, Ames, Iowa 50011

Received May 31, 1983

Numerous polyatomic anions and cations of the post-transition elements are now known,[2] all of which exhibit the customary diamagnetism. And while the known Sn_5^{2-} [3] (D_{3h}) and Sn_9^{4-} [4] (C_{4v}) have the expected closo and nido configurations for $2n + 2$ (12) and $2n + 4$ (22) electrons, respectively, the Bi_9^{5+} ion[5] isoelectronic with the latter instead adopts a closo D_{3h} geometry. Various reasons for this exception have been proposed.[6,7] This closo configuration is customarily associated with nine-atom 20-electron species, and although the corresponding Sn_9^{2-} is not known, the analogous $TlSn_8^{3-}$ [8] and Ge_9^{2-} [6] anions do behave as expected. We report here the formation of the first paramagnetic cluster, Sn_9^{3-}, that with 21 skeletal electrons and D_{3h} symmetry also provides direct evidence regarding the anomalous Bi_9^{5+} configuration.

An alloy of stoichiometry KSn_2 reacts with 2,2,2-crypt[9] in ethylenediamine under appropriate reaction conditions to produce a dark red solution that, upon solvent removal, deposits black plates of $(2,2,2\text{-crypt-}K^+)_3Sn_9^{3-}\cdot 1.5en$. Shorter reaction times (<2 days) produce an unknown monoclinic phase while longer periods (>3 weeks) yield a triclinic phase which may be $(\text{crypt-}K^+)_4Sn_9^{4-}$ (only the crypt-Na^+ salt is known[4]).

Crystal data: space group $P\bar{1}$, $a = 15.002$ (1) Å, $b = 21.794$ (2) Å, $c = 14.060$ (1) Å, $\alpha = 99.770$ (10)°, $\beta = 101.595$ (9)°, $\gamma = 89.694$ (10)°, $V = 4435.9$ (7) Å^3, and $Z = 2$. A total of 13 229 reflections in one hemisphere with $2\theta < 45°$ were collected at −60 °C using a four-circle automated diffractometer (Mo Kα radiation). The compound is nearly isostructural with $(2,2,2\text{-crypt-}K^+)_3(TlSn_8^{3-}\text{-}TlSn_9^{3-})_{1/2}\cdot en$,[8] with nine tin atoms in essentially the atom positions as in $TlSn_8^{3-}$ but with no electron density at the tenth (thallium) position in $TlSn_9^{3-}$ (D_{4d}). The final block diagonal least-squares refinement yielded $R = 0.085$ and $R_w = 0.125$ for 9293 independent reflections ($I > 3\sigma(I)$), 96 non-hydrogen atoms and anisotropic thermal parameters for the Sn and K atoms.

With six crypt-K^+ cations and two anion clusters per cell the anion is presumed to have a 3− charge, and ESR and magnetic susceptibility measurements confirm the paramagnetic character of the compound. ESR spectra of the bulk reaction product, a single crystal (in unknown orientation), and a frozen solution (crystals redissolved in en) measured between 298 and 4 K all show a strong resonance with two g values, ~1.97 and ~2.07, as expected for an axially symmetric species. The starting alloy KSn_2 gives no ESR signal. Room-temperature ESR of either a solution of crystals in en (as above) or one from which crystals may be grown both exhibit a single resonance ($g \cong 2.03$), again as expected. Magnetic susceptibilities of the compound measured on a Faraday balance yield a linear Curie–Weiss behavior from 298 to 100 K, with $\mu_{eff} = 1.38$ and $\chi_{mol} = 5.56 \times 10^{-3}$ emu at 298 K (after diamagnetic correction). ^{117}Sn and ^{119}Sn NMR spectra have been run on solutions of KSn_2 and crypt in both en and liquid NH_3.[10] The latter shows only the known Sn_9^{4-} multiplet resonance.[11] However, the en solution exhibits an *extremely* broad signal (fwhm ~ 1100 Hz) with a chemical shift appropriate for Sn_9^{4-} (−1230 ppm from $(Me)_4Sn$), the broadening presumably arising from relaxation by the paramagnetic Sn_9^{3-} anion.

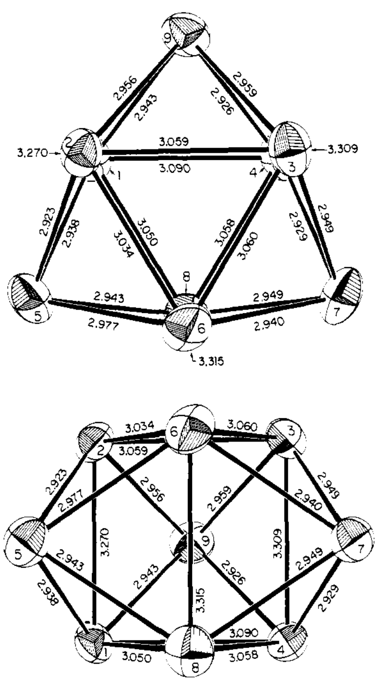

Figure 1. Two views of the Sn_9^{3-} anion. Thermal ellipsoids are shown at the 50% probability level ($\sigma_d = 0.002$ Å for all distances).

Table I. D_{3h} Nine-Atom Clusters

cluster	skeletal e's	h:e	ref
Bi_9^{5+}	22	1.15	5
Sn_9^{3-}	21	1.08	
$B_9H_9^{2-}$	20	0.97	14
$TlSn_8^{3-}$	20	1.01^a	8
$Ge_9^{2-\,b}$	20	1.06^a	6

^{a} One long distance for the prism height was omitted in this calculation; otherwise the values are 1.03 and 1.10. ^{b} Distorted to C_{2v}.

The Sn_9^{3-} anion shown in Figure 1 deviates very little from an ideal tricapped trigonal prismatic (D_{3h}) configuration. The thermal ellipsoids are relatively small and spherical compared with similar structures and show *no* indication of the disorder expected were a 50:50 mixture of Sn_9^{2-} and Sn_9^{4-} ions to occupy the same site. The Sn_9^{3-} cluster has average values of 3.298 Å, 3.058 Å, and 2.944 Å for the height (h) and edge (e) of the trigonal prism and from the prismatic to the capping (c) atoms, respectively. The height to edge ratio (h:e) of D_{3h} nine-atom clusters provides the best correlation of configuration with electron count.[6,7,12,13] As can be seen in Table I, h:e for the 21-electron Sn_9^{3-} is exactly intermediate between that for 20- and 22-electron clusters.

Extended Hückel MO calculations bear out these observations; Sn_9^{2-}, Sn_9^{3-}, and Sn_9^{4-} models were considered, each one for three idealized D_{3h} configurations with h:e:c = 3.12:3.16:2.96 (Å) (as in $TlSn_8^{3-}$), 3.30:3.06:2.94 (Sn_9^{3-}), and 3.45:2.99:2.93 (proportioned similar to Bi_9^{5+}). The appropriate elongation for each electron count did indeed produce the largest total (one-electron) energy and the greatest HOMO–LUMO gap (admittedly differences between some configurations are hardly significant). The

---

(1) Operated for the U.S. Department of Energy by Iowa State University under contract No. W-7405-Eng-82. This research was supported by the Office of Basic Energy Sciences, Material Sciences Division.

(2) Corbett, J. D.; Critchlow, S. C.; Burns, R. C. *ACS Symp. Ser.* **1983**, *232*.

(3) Edwards, P.; Corbett, J. D. *Inorg. Chem.* **1977**, *16*, 903–907.

(4) Corbett, J. D.; Edwards, P. *J. Am. Chem. Soc.* **1977**, *99*, 3313–3317.

(5) Friedman, R. M.; Corbett, J. D. *Inorg. Chem.* **1973**, *12*, 1134–1139.

(6) Belin, C. H. E.; Corbett, J. D.; Cisar, A. *J. Am. Chem. Soc.* **1977**, *99*, 7163–7169.

(7) Burns, R. C.; Gillespie, R. J.; Barnes, J. A.; McGlinchey, M. J. *Inorg. Chem.* **1982**, *21*, 799–807.

(8) Burns, R. C.; Corbett, J. D. *J. Am. Chem. Soc.* **1982**, *104*, 2804–2810.

(9) 4,7,13,16,21,24-hexaoxa-1,10-diazobicyclo[8.8.8]hexacosane, $N(C_2H_4OC_2H_4OC_2H_4)_3N$.

(10) Burns, R. C., private communication, 1982.

(11) Rudolph, R. W.; Wilson, W. L.; Parker, F.; Taylor, R. C.; Young, D. C. *J. Am. Chem. Soc.* **1978**, *100*, 4269.

(12) Wade, K.; O'Neill, M. E. *J. Mol. Struct.*, in press.

(13) Wade, K.; O'Neill, M. E. *Polyhedron*, submitted for publication.

(14) Guggenberger, L. J. *Inorg. Chem.* **1968**, *7*, 2260–2264.

0002-7863/83/1505-5715$01.50/0

LUMO for 20-electron and the HOMO for 21- and 22-electron D_{3h} clusters here and in Bi_9^{5+}[15] are of a_2'' symmetry and are strongly σ antibonding along the height, pi bonding for the edges, and weakly bonding to the capping atoms. Thus the changes in *h*:*e* observed on occupation of $2a_2''$ with one or two electrons come partly from an increase in height and partly from a decrease in the edges of the trigonal prism and, again, Sn_9^{3-} is appropriately intermediate. The undiscovered Sn_9^{2-} (D_{3h}) may have low stability as the LUMO $2a_2''$ is calculated to be only 1.6 eV above the HOMO.

The alternative nido unicapped square antiprism (C_{4v}) is preferred for 22e in Sn_9^{4-} according to similar calculations. A C_{4v} symmetry is not feasible for Sn_9^{2-} or Sn_9^{3-} as these would have HOMO configurations of e^2 or e^3, respectively.

Further details and discussion will be provided in a later complete article.

Acknowledgment. We thank Dr. Robert C. Burns for many valuable discussions and the NMR data.

Supplementary Material Available: Listings of positional and thermal parameters and structure factor amplitudes (25 pages). Ordering information is given on any current masthead page.

---

(15) Corbett, J. D.; Rundle, R. E. *Inorg. Chem.* **1964**, *3*, 1408–1412.

Book Reviews

The Chemistry of Chalcones and Related Compounds. Edited by D. N. Dhar (Indian Institute of Technology, Kanpur). John Wiley & Sons, New York. 1981. xiii + 285 pp. $38.50.

This book is the first comprehensive literature survey to be made concerned with the study of chalcones and related compounds. It reports on the current trends in the rapidly expanding field of chalcone chemistry. The text is organized into four major parts that are subdivided into three, fourteen, seven, and five chapters, respectively.

Part one deals with the synthetic methods for chalcone, substituted chalcones, and heterocyclic chalcone analogues, as well as their mechanism of formation. Referring to part two, it consists of fourteen chapters, illustrating reactions of chalcones with reducing and oxidizing agents, ketones, esters, amides, cyanides, isocyanates, amines, organometallics, halogens, cyclization reactions, both chemically and biochemically, polarographic studies, and photochemical and miscellaneous reactions. Part three is devoted to the physical properties of chalcones and their heterocyclic analogues. This part is broken down into seven chapters. The main characteristic features of this part are spectroscopic, X-ray crystallographic, and dipole measurement studies. Part four spreads over five chapters. It includes naturally occurring, biologically active chalcones and their derivatives. Their uses as sweeteners, stabilizers, photosensitive materials, polymers, scintillators, analytical reagents, polymerization catalyst, fluorescent agents, and organic brightening additives are also discussed. Furthermore, it deals with synthesis and reactions of chalcone epoxides and chalcone α,β-dibromides, which serve as useful precursors, in the field of organic synthesis. Most chapters are well organized and provide a convenient outline to their specific content. But, it would be more reasonable if part one includes the last two chapters (27 and 28) of part four. Structural examples are used liberally throughout the book. There are few typographical errors (the arrow in between compounds XXVIIIa and XXX should include phenylhydrazine, among the reagents in the scheme, depicted on page 126). In spite of some details against which objections are raised, the book is well organized, composed with clarity, and should serve well the purpose for which it was written.

In summary, I think the editor has done a creditable job of compiling the chemical research in the field of chalcone chemistry. It is highly recommended as a reference book for all investigators looking for an overview of chalcone chemistry.

Hanafi H. Zoorob, *El-Mansoura University*

The Literature Matrix of Chemistry. By Herman Skolnik (Hercules Inc.). John Wiley & Sons, New York. 1982. xi + 297 pp. $30.00.

Since the chemical literature has grown tremendously in recent years, it is obvious that some plan for searching it adequately is of paramount importance. Such a plan is especially desirable today when formal courses on searching are offered in few, if any, chemistry and chemical engineering departments. The author, Dr. Herman Skolnik, as editor of the *Journal* of *Chemical Information and Computer Science* since 1961, is highly qualified to write such a book and he has succeeded admirably in the task.

Dr. Skolnik's treatment is more comprehensive than former ones on the subject. It covers books, encyclopedias, treatises, data compilations, patents, journals, secondary publications, chemical abstracts service, other indexing/abstracting services, and computer-based information services. It is not a dry tabulation of what is available since it gives interesting sidelights on how the searching has changed as more aids have become available.

Perhaps the most interesting chapter in the book is that of the Chemical Abstracts Service. *Chemical Abstracts* is unique in that it is without a peer in its approach to the literature of chemistry and chemical engineering. With its great variety of indexes it is rare that known chemical information will not become available to the competent searcher.

This book is a *must* for the serious student of the chemical sciences.

Calvin A. Buehler, *University of Tennessee*

Acetylene-Based Chemicals from Coal and Other Natural Resources. Volume 6. Chemical Industries Series. By Robert J. Tedeschi (Tedeschi and Associates, Inc.). Marcel Dekker, New York. 1982. viii + 221 pp. $39.50.

This book presents a practical and concise overview of the production technology and commercial applications related to acetylene and its derivatives. It is divided into two chapters. Chapter I discusses acetylene with respect to its production from coal, natural gas, and oil feed stocks, and its recovery, purification, stability, and handling. The production of commodity chemicals derived form acetylene–acetylene black, acrylic acid and esters, acrylonitrile, acetaldehyde, chloroprene, isoprene, vinyl chloride, and vinyl acetate is also discussed. Emphasis is placed on both raw materials for these chemicals and technological and application information. Although most of these chemicals are currently manufactured from routes other than acetylene, the author contends that acetylene made from coal via the calcium carbide route may compete favorably in the future. In Chapter II, the production with use of Reppe technology of specialty acetylenic chemicals such as propargyl alcohol, 2-butyn-1,4-diol, butane-1,4-diol, tetrahydrofuran, γ-butyrolactone, 2-pyrrolidone and its derivatives, as well as several secondary and tertiary acetylenic alcohols, is discussed. The applications of these chemicals in areas such as flavors, drugs, pesticides, surfactants, corrosion inhibitors, polymers, etc. are also mentioned.

This book is well organized and contains many flow diagrams of important commercial processes. The unique blend of research, technology, and business transactions in this book should make it a very useful reference book to industrial acetylenic chemicals.

Shang-Shing P. Chou, *Fu Jen University*

The Alkaloids. Senior Reporter: M. F. Grundon (New University of Ulster). The Royal Society of Chemistry, London, England. 1982. xii + 320 pp. $55.00.

This Specialist Periodical Report is Volume 12 in the series dealing with alkaloids and reviews the literature for the period July 1980 through June 1981. The whole of the literature for that period, with the exception of that dealing with the *Lycopodium* alkaloids, has been examined by the 17 reporters with their usual *elan vital* and care, making this volume, as was its predecessors, indispensable to individuals involved in the study of alkaloid chemistry. As is customary, chemistry, isolation, synthesis, and biosynthesis are emphasized rather than biological properties. Also, as is customary, there is only an author index and there is extensive use of footnoted references to previous volumes in the series. However, as is not usual, the art for one-third of the chapters was produced from camera-ready copy. The minor variation in type font between art and text has not reduced the quality of the production and, indeed, it is relatively error free.

D. R. Dalton, *Temple University*