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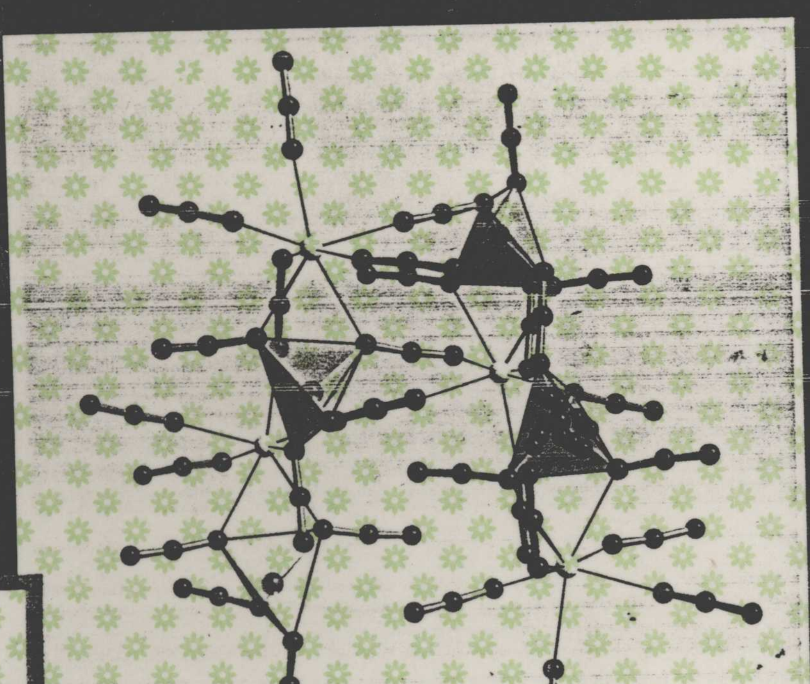
Inorganic Chemistry Highlights

Edited by Gerd Meyer,
Dieter Naumann, Lars Wesemann



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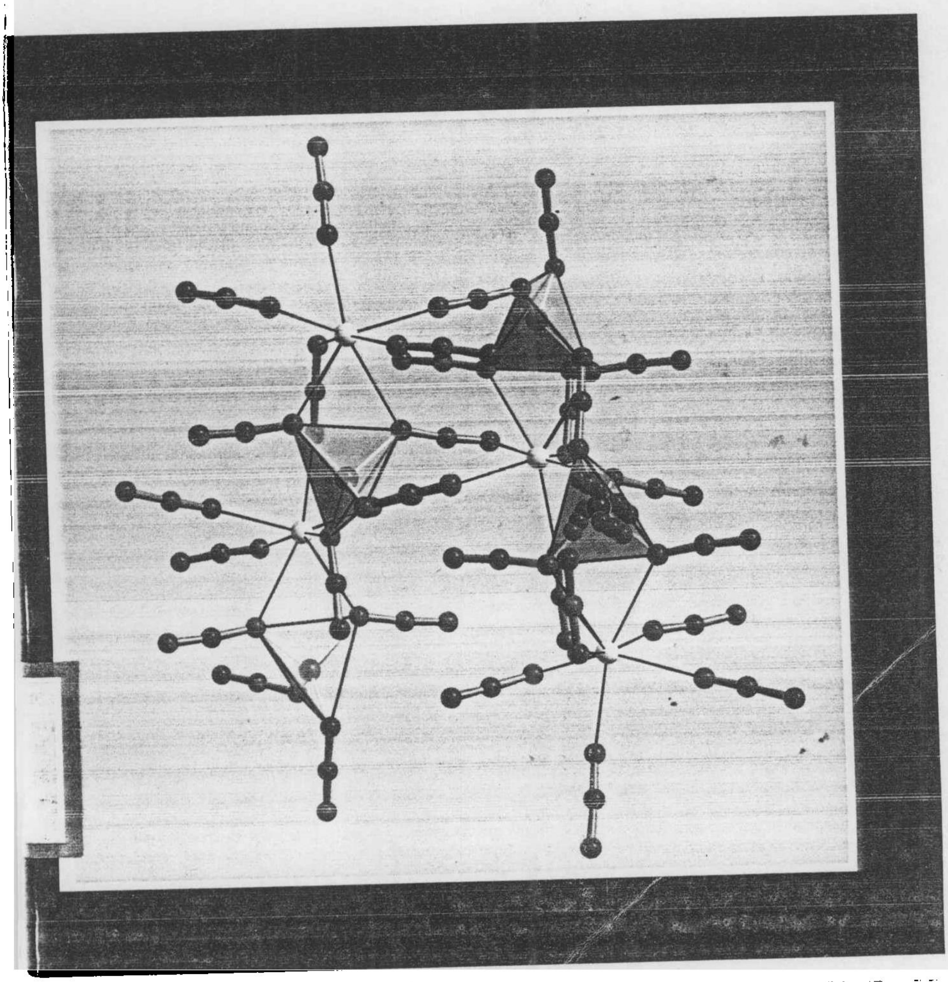

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Editors

Prof. Dr. Gerd Meyer
Prof. Dr. Dieter Naumann,
Prof. Dr. Lars Wesemann
Institut für Anorganische Chemie
der Universität zu Köln
Greinstraße 6
D-50939 Köln
Germany

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Preface

Highlights from all areas of chemistry are a well established section in Angewandte Chemie, whilst Organic Synthesis Highlights represents a successful Wiley-VCH book series. We are now proud to present the first volume of Inorganic Chemistry Highlights. May it become another model in a successful product line.

The nineteen articles that we have drawn together for this volume of highlights cover a wide range of inorganic chemistry. Our survey begins with physical and theoretical inorganic chemistry relating to Zintl compounds, together with attempts to predict crystal structures from scratch. A substantial article devoted to cation conductors is followed by the spectacular giant ring-shaped polyoxometalate "clusters" and molybdenum peroxo complexes, both potential and capable heterogeneous catalysts. Rare earth organometallics and related coordination compounds, also important as potential catalysts, are the subjects of two further articles. Further highlights in the area of inorganic coordination chemistry are represented by enzymes as giant bioinorganic molecules and by metalla-calix[4]arenes. We continue with complex compounds and metal carbonyl cations as superelectrophiles; borylenes and silaboranes then lead on to molecular clusters of low-valent main group element compounds: carbaalanes and aluminium and gallium subhalides. From the area of typical main group chemistry there are covalent main group azides and silacalix-[n]-phosphinines as sp^2 phosphorous equivalents of CO matrices. Nitrogen fixation – or, in other words, utilization of dinitrogen as a raw material – is an important modern basic research topic, offering the potential, after some 100 years, to revolutionize the production of ammonium compounds and nitrates. The volume concludes with new organoxenon chemistry, highlighting one area in the recent renaissance in noble gas chemistry.

This first volume by no means covers the entire wealth of inorganic chemistry, nor are the highlights collected together here by any means the *sole* highlights of inorganic chemistry at present. We therefore hope that this first volume of Inorganic Chemistry Highlights will be well received, and that those of our colleagues who were unable to contribute for various reasons, and others yet to be approached, will feel encouraged to put forward further highlights for future volumes.

Köln, September 2001

Gerd Meyer
Dieter Naumann
Lars Wesemann

List of Authors

Gin-ya Adachi
Department of Applied Chemistry
Faculty of Engineering
Osaka University
2-1 Yamadaoka, Suita
Osaka 565-0871
Japan

Friedhelm Aubke
Department of Chemistry
University of British Columbia
2036 Main Mall
Vancouver, B. C., V6T 1Z1
Canada
e-mail: aubke@chem.ubc.ca

Holger Braunschweig
Department of Chemistry
Catalysis and Advanced Materials Section
Imperial College, London
South Kensington
Exhibition Road
GB-London SW7 2AY
United Kingdom
e-mail: h.braunschweig@ic.ac.uk

Wonyoung Choe
Department of Chemistry
Iowa State University
Ames
Iowa 50011
USA

Leroy Cronin
School of Chemistry
University of Birmingham
Edgbaston,
GB-Birmingham B15 2TT
United Kingdom
e-mail: L.Cronin@bham.ac.uk

Glen B. Deacon
School of Chemistry
Monash University
Wellington Road
Clayton
Victoria 3800
Australia
e-mail: g.deacon@sci.monash.edu.au

Pascal Le Floch
Laboratoire Heteroelements et Coordination
UMR CNRS 7653
Ecole Polytechnique
F-91128 Palaiseau Cedex
France
e-mail: lefloch@mars.polytechnique.fr

Carlo Floriani
Department of Chemistry, BCH 3307
University of Lausanne
CH-1015 Lausanne
Switzerland
e-mail: carlo.floriani@icma.unil.ch

Craig M. Forsyth
School of Chemistry
Monash University
Wellington Road
Clayton
Victoria 3800
Australia

Wolfgang Fraenk
Department Chemie
Universität München
Butenandtstraße 5–13 (Haus D)
D-81377 München
Germany
e-mail: fwp@cup.uni-muenchen.de

Sandro Gambarotta
Department of Chemistry
University of Ottawa
Ottawa
Ontario
Canada
e-mail: sgambaro@science.uottawa.ca

Carsten Gerdemann
Anorganisch-Chemisches Institut
Westfälische Wilhelms-Universität
Wilhelm-Klemm-Straße 8
D-48149 Münster
Germany

Nobuhito Imanaka
Department of Applied Chemistry
Faculty of Engineering
Osaka University
2-1 Yamadaoka, Suita
Osaka 565-0871
Japan
e-mail: imanaka@ap.chem.eng.osaka-u.ac.jp

Martin Jansen
Max-Planck-Institut für Festkörperforschung
Heisenbergstraße 1
D-70569 Stuttgart
Germany
e-mail: martin@jansen.mpi-stuttgart.mpg.de

Thomas M. Klapötke
Department Chemie
Universität München
Butenandtstraße 5–13 (Haus D)
D-81377 München
Germany
e-mail: tmk@cup.uni-muenchen.de

Christoph Klemp
Institut für Anorganische Chemie
Universität Karlsruhe
Engesserstraße, Geb. 30.45
D-76128 Karlsruhe
Germany
e-mail: klemp@achpc9.chemie.uni-karlsruhe.de

Bernt Krebs
Anorganisch-Chemisches Institut
Westfälische Wilhelms-Universität
Wilhelm-Klemm-Straße 8
D-48149 Münster
Germany
e-mail: krebs@uni-muenster.de

Chi-Shen Lee
Department of Chemistry
Iowa State University
Ames
Iowa 50011
USA

Willem van der Lugt
Solid State Physics Laboratory
University of Groningen
Nijenborgh 4
NL-9747 AG Groningen
The Netherlands

François Mathey
Laboratoire Heteroelements et Coordination
UMR CNRS 7653
Ecole Polytechnique
F-91128 Palaiseau Cedex
France

Gerd Meyer
Institut für Anorganische Chemie
Universität zu Köln
Greinstraße 6
D-50939 Köln
Germany
e-mail: gerd.meyer@uni-koeln.de

Nicolas Mézailles
Laboratoire Heteroelements et Coordination
UMR CNRS 7653
Ecole Polytechnique
F-91128 Palaiseau Cedex
France

Gordon J. Miller
Department of Chemistry
Iowa State University of Science and Technology
Gilman Hall
Ames
Iowa 50011
USA
e-mail: gmiller@iastate.edu

Dieter Naumann
Institut für Anorganische Chemie
Universität zu Köln
Greinstraße 6
D-50939 Köln
Germany
e-mail: d.naumann@uni-koeln.de

Peter W. Roesky
Institut für Anorganische Chemie der Universität Karlsruhe
Engesserstraße 15
D-76128 Karlsruhe
Germany
e-mail: roesky@achibm6.chemie.uni-karlsruhe.de

Annette Rompel
Anorganisch-Chemisches Institut
Westfälische Wilhelms-Universität
Wilhelm-Klemm-Straße 8
D-48149 Münster
Germany

Hansgeorg Schnöckel
Institut für Anorganische Chemie
Universität Karlsruhe
Engesserstraße, Geb. 30.45
D-76128 Karlsruhe
Germany

J. Christian Schön
Max-Planck-Institut für Festkörperforschung
Heisenbergstraße 1
D-70569 Stuttgart
Germany
e-mail: schoen@c3serv1.mpi-stuttgart.mpg.de

Werner R. Thiel
Institut für Chemie
Technische Universität Chemnitz
Straße der Nationen 62
D-09107 Chemnitz
Germany

Wieland Tyrra
Institut für Anorganische Chemie
Universität zu Köln
Greinstraße 6
D-50939 Köln
Germany

Werner Uhl
Fachbereich Chemie
Philipps Universität Marburg
Hans-Meerwein-Straße
D-35032 Marburg
Germany
Telefax: Int. +6421/282-5653
e-mail: uhl@chemie.uni-marburg.de

Peter Verkerk †
Interfakultaire Reactor Instituut
Delft University of Technology
NL-2629 JB Delft
The Netherlands

Andreas Vogel
Anorganisch-Chemisches Institut
Westfälische Wilhelms-Universität
Wilhelm-Klemm-Straße 8
D-48149 Münster
Germany

Lars Wesemann
Institut für Anorganische Chemie
Universität zu Köln
Greinstraße 6
D-50939 Köln
Germany
e-mail: lars.wesemann@uni-koeln.de

Helge Willner
Anorganische Chemie
Gerhard Mercator Universität Duisburg
Lotharstraße 1
D-47057 Duisburg
e-mail: willner@uni-duisburg.de

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1
Molten Zintl Alloys

Willem van der Lugt and Peter Verkerk

1.1
Introduction and some Terminology

Molten Zintl phases make up an interdisciplinary research subject with three main components: the crystal chemistry of Zintl ions, the physics of liquids, and the theory of electrons in disordered materials. An important objective of this contribution is to amalgamate these three disciplines.

Zintl ions are polyanions formed by anion clustering in ionic alloys. We distinguish between two categories: those that fit the so-called Zintl–Klemm concept and those that are electron-deficient.

In the Zintl–Klemm compounds relevant to this paper, an electronegative atom belonging to group *n* in the periodic table accepts one electron from its electropositive companions and thereby acquires the valence electron configuration typical for neutral atoms of the group n+1. Accordingly, the polyanions formed are similar to molecules of the elements of group n+1. The Zintl–Klemm ions are octet compounds with 2c–2e bonds. Examples of alloys dealt with in this paper are KPb, RbPb, and CsPb, with tetrahedral $(Pb_4)^{4-}$ Zintl ions analogous to P_4 and As_4[1]. Likewise, KSn, RbSn, and CsSn form $(Sn_4)^{4-}$ Zintl ions[2]. In NaSb, KSb, RbSb, and CsSb, tellurium-like, infinite Sb-chains can be discerned[3], while KTe forms $(Te_2)^{2-}$ dimers similar to halogen molecules[4]. The behavior of alkali–bismuth alloys is slightly more complicated.

Examples of electron-deficient structures are provided by the A_8Tr_{11} compounds, with $(Tr_{11})^{7-}$ polyanions (A = K, Rb, Cs, Tr = Tl, In, Ga; not all the possible combinations of A and Tr are seen)[5]. An electron pair can be shared by more than two atoms. We note that $(Tl_6)^{6-}$ ions have also been found[6]. All the Zintl ions mentioned above are discrete. For further information on the structure and bonding of Zintl alloys the reader is referred to a number of reviews[7].

What can we expect to find when a highly structured crystal such as a Zintl phase melts? No perfect Zintl ions, but we may hope for some fingerprints left by them. The liquid state is "the awkward-in-between"[8]. Neither the completely disordered gas phase nor the well ordered solid state offers an ideal system of reference, and recourse to rather poorly defined notions and to analogies is often necessary. There are, however, indications that considerable order exists in liquid Zintl alloys up to