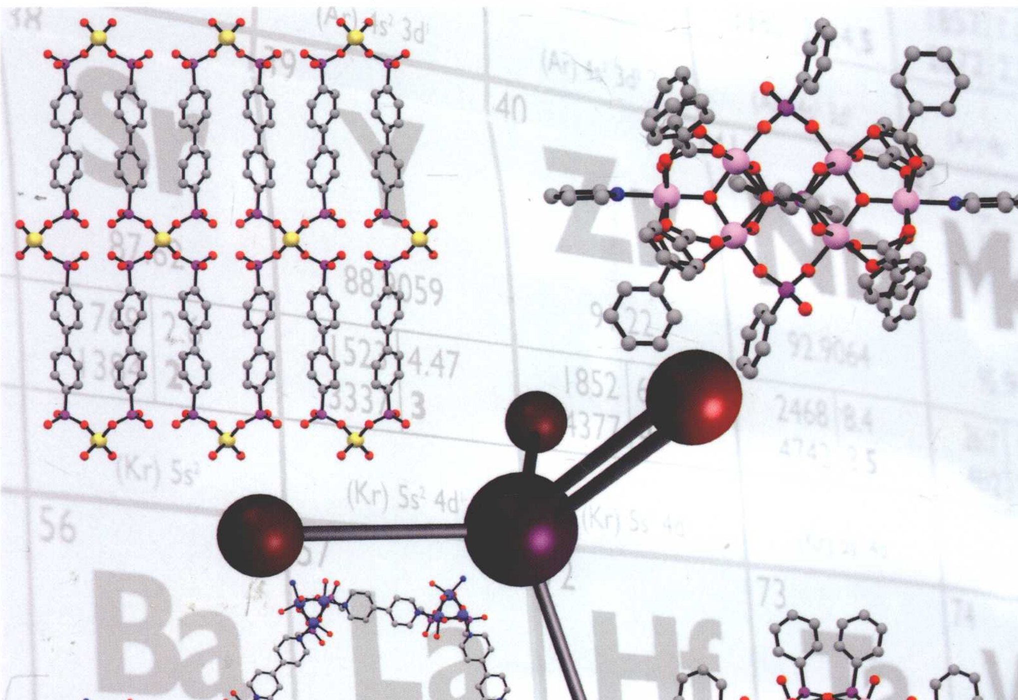
Edited by Abraham Clearfield and Konstantinos D. Demadis

Metal Phosphonate Chemistry

From Synthesis to Applications



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From Synthesis to Applications

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Preface

In Chapter 1 it is stated that Giulio Alberti *et al.* were the first to publish on metal phosphonates, by reporting on compounds of the formula $Zr(O_3PR)_2$, where R is an alkyl or aryl group ("Crystalline $Zr(R\text{-}PO_3)_2$ and Zr-$(R\text{-}OPO_3)_2$ compounds (R = organic radical): New class of materials having layered structure of zirconium-phosphate type", G. Alberti, U. Costantino, S. Allulli, N. Tomassini, *J. Inorg. Nucl. Chem.,* 1978, **40**, 1113). However, almost simultaneously Cunningham *et al.* published a paper on divalent metal phosphonates ("Divalent metal phenylphosphonates and phenylarsonates", D. Cunningham, P.J.D. Hennelly, T. Deeney, *Inorg. Chim. Acta.,* 1979, **37**, 95). Although, they reported on a number of properties of these compounds their structures were not determined. Due to the very poor X-ray patterns of the zirconium compounds, Alberti did not publish the structures; however, he did draw up a model showing a bilayer of phenyl groups between the ZrO_6P_2 inorganic layers. This model served as a guide for the dozens of subsequent zirconium phosphonates that were synthesized. Sulfonation of the phenyl groups in 1987 ("The preparation and ion-exchange properties of zirconium sulfophosphonates", C. Y. Yang, A. Clearfield, *React. Polym.,* 1987, **5**, 13) and their subsequent exfoliation proved the layered nature of these compounds and years later we were able to solve the crystal structure of the phenyl compound from a highly crystalline powder prepared by the Alberti group ("Determination of crystal structures from limited powder data sets: Crystal structure of zirconium phenylphosphonate", D. M. Poojary, H.-L. Hu, F. L. Campbell, III, A. Clearfield, *Acta Cryst. B,* 1993, **49**, 996). The structure was as predicted except that the phenyl rings are tilted about 30° from the perpendicular. Another milestone occurred in 1988 with the synthesis and structure determination of a number of transition metal phenyl phosphonates by

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Mallouk ("Synthesis and structural characterization of a homologous series of divalent-metal phosphonates, $M^{II}(O_3PR)\cdot H_2O$ and $M^{II}(HO_3PR)_2$", G. Cao, H. Lee, V. M. Lynch, T. E. Mallouk, *Inorg. Chem.*, 1988, **27**, 2781). Because of the one to one ratio of phosphonate groups to metal ions there are half as many oxygen atoms to coordinate to the metal. Nevertheless the 6-coordination was accomplished by chelation of the metal by phosphonate groups above and below with donation of electron pairs by the chelating oxygens to adjacent metal atoms. The third phosphonate oxygens bonded across these chains to form layers and the sixth metal orbital is occupied by a water molecules. In Chapter 1, it is also shown that Group I cations from Li^+ to Cs^+ bond to 4,4′-diphosphonic acids with increasing coordination from 4 to 8 with exactly the same composition. All of this demonstrates the versatility of phosphonic acids as ligands.

From these beginnings and many other interesting features of metal phosphonate chemistry published before 1990 it was realized, as some of the early pioneers remarked, "that a vast new field was developing." A huge number of organic moieties can be converted to phosphonic acids, allowing for a vast array of metal phosphonates to be synthesized. Thus, like a rolling snowball descending a mountain the publications grew and grew, as shown in Figure 1.

In 2009 I was contacted by the Royal Society of Chemistry to consider a book on metal phosphonate chemistry. Yes, I thought it was a good idea but the amount of work required was daunting. Shortly after that I attended the 1st International Conference on Multifunctional, Hybrid and Nanomaterials, in Tours, France, and there I met Kostas Demadis for the first time. At lunch with him, I mentioned the book idea. Kostas thought it was great idea and right then and there the decision to go forward with it was made. So here we were a duo of apostates in an ocean of metal-carboxylate chemists plotting heresy. The comfort of having a young enthusiastic co-editor

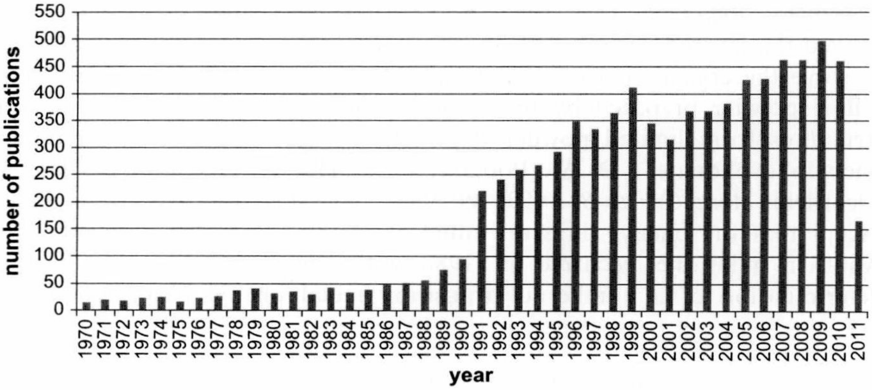

Figure 1 Graph with number of publications per year in the "phosphonate" field (source Thomson ISI, May 5, 2011).

whose English was perfect clinched the deal. We both drew up a list of potential authors, all leaders in their respective expertise and made our contacts. The result is now before you! The quality of the authors and the variety of areas covered make this a very special offering. The book is diverse in the chapter topics (a quick look at the Table of Contents will convince the reader), well referenced and with some amazing illustrations. Kostas and I wish to thank the authors for a job well done and I am indebted to Kostas as he not only edited half the chapters but he picked up the ball when I faltered and assembled all the chapters in the required way and transmitted them to our RSC publishers.

Abraham Clearfield
Texas A&M University
College Station, USA

and

Kostas D. Demadis
University of Crete
Heraklion, Greece

Abraham Clearfield

"I am pleased to dedicate this book to my wife Ruth who urged me to go on for a PhD and has been a steady supporter and life-long help mate. What more could anyone ask for?"

Kostas Demadis

"This book is dedicated to several people who directly or indirectly, knowingly or unknowingly contributed to its completion: my wife Foteini for emotional support, my students who give purpose to our research, Wilhelm Conrad Röntgen for inventing X-rays, and Lemmy Kilmister for inspiration."

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