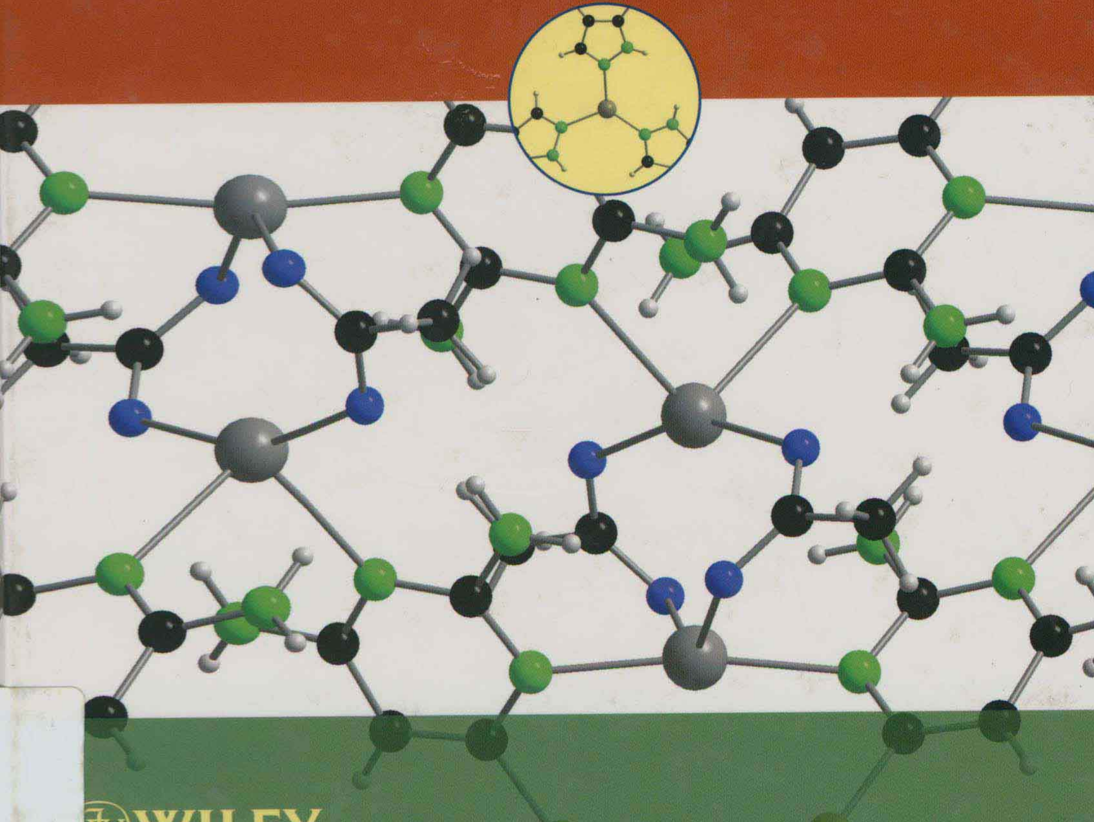
DESIGN AND CONSTRUCTION OF COORDINATION POLYMERS

EDITED BY

MAO-CHUN HONG

LING CHEN



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Dedicated to

the Fujian Institute of Research on the Structure of Matter,
Chinese Academy of Sciences, on the occasion of
the fiftieth anniversary of its founding
and
Professor Xin-Tao Wu, one of the pioneers in the
development of the Fujian Institute, on the
occasion of his seventieth birthday

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PREFACE

This volume, *Design and Construction of Coordination Polymers*, is published in recognition of the fiftieth anniversary of the beginning of the Fujian Institute of Research on the Structure of Matter, Chinese Academy of Science, and is dedicated to Prof. Xin-Tao Wu, on the occasion of his seventieth birthday. The volume contains 13 chapters that focus on this theme, contributed by former graduates and friends of this institution. They span a wide range of topics, systems, and approaches to coordination polymers. In Chapter 1, G. Meyer and co-workers describe a variety of AgL_1L_2 coordination complexes achieved with mixed N-containing ligands, some of which exhibit particularly short Ag–N distances. A series of indium(III)–carboxylate coordination polymers with a variety of dimensionalities are reported in Chapter 2 by M.-C. Hong and colleagues. Following this, in Chapter 3, X.-M. Chen and co-workers examine an interesting series of coordination polymers that are formed by solvothermal reactions between diverse metals and ligands, covering a variety of functionalities and reaction types. In Chapter 4, C.-Z. Lu and co-workers report on a variety of hybrid polyoxometallates built of oxo-Mo, oxo-Cu, and oxo-Ag centers and 1,2,4-triazolate or pyridine derivatives. In Chapter 5, C.-Y. Su and others describe the range of Ag(I) coordination environments that can be obtained with various ligand types as well as interpenetrating polymers and their diverse properties and applications. A different type of variety results when coordination polymers are tuned via systematic variations in the bridging organic backbones within multidentate ligands, as related by X.-H. Bu and others in Chapter 6.

Chapter 7, by R.-G. Xiong and co-workers, features a different direction, the design and synthesis of ferroelectric coordination compounds or polymers that are constructed of monochiral ligands and occur in polar space groups. The generation and properties of paramagnetic solids of different dimensionalities from three-atom bridging ligands and 3d metal ions are described by S. Gao and colleagues in Chapter 8. In Chapter 9, L.-M. Wu and L. Chen describe and explain structural, optical, and thermal properties of various iodometallic phases of Pb or Bi with different dimensionalities and motifs. J.-P. Lang and co-workers relate in Chapter 10 the design, construction, and optical properties of supramolecular cluster-based phases of Mo(W)/Cu/S. Microporous metal–organic frameworks as materials for gas storage and separation are addressed in Chapter 11 by J. Li and colleagues. In Chapter 12, H.-C. Zhou and co-workers enumerate the design, construction, and properties of various metal–organic frameworks for storage and separation of gases, H_2 in particular. Finally, in Chapter 13, Z.-W. Mao and colleagues outline the application of some bioinorganic coordination compounds as mimics or models for a range of biological functions or therapeutic agents. Enjoy!

We are grateful for all the authors who unselfishly spent their most precious time in writing contributions for the volume and meeting deadlines. Special thanks are given to Prof. Thomas C. W. Mak at the Chinese University of Hong Kong, Prof. Bei-Sheng Kang at Sun Yat-Sen University, Guangzhou and Prof. Qiu -Tian Liu at FIRSM for their kind help, and A. Lekhwani and R. Amos of John Wiley & Sons, Inc. for editorial assistance.

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CONTENTS

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COORDINATIVE FLEXIBILITY OF MONOVALENT SILVER IN $[Ag^I \leftarrow L1]L2$ COMPLEXES

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1.1 INTRODUCTION

Monovalent silver, Ag^+, is a fifth-period closed-shell d^{10}-ion. It is therefore often considered a pseudo-alkali-metal cation with an ionic radius close to that of Na^+, 114 versus 113 pm for coordination number (CN) 4 [1]. Indeed, AgCl crystallizes with an NaCl type of structure, with $a = 554.9$ versus $a = 563.9$ pm [2]. On the other hand, many physical properties are quite different. One striking example is that of AgCl and NaCl solubilities in water, 1.88×10^{-3} g/L versus 358 g/L [3]. The solubility of AgCl is enhanced dramatically through the addition of aqueous ammonia, and linear $[Ag(NH_3)_2]^+$ cations are formed. Quite obviously, there is a much larger affinity of Ag^+ toward the N-donor ligand ammonia than toward water or chloride as competing ligands.

There are many complex salts of the $[Ag(NH_3)_2]^+$ cation with common inorganic cations, NO_3^- or ClO_4^- (see, e.g., ref. 4). In $[Ag(NH_3)_2](ClO_4)$, the $[H_3N–Ag–NH_3]^+$ complex cation is linear by symmetry in both the high- and low-temperature modifications [4d]. The Ag–N distances are 214 pm, on average, at 170 K. The cations are arranged such that the shortest Ag–Ag contacts are 302 pm, well above the Ag–Ag distance of 288.9 pm in metallic silver but below the sum of the

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van der Waals radii of 344 pm. However, *argentophilicity* [5] (i.e., d^{10}–d^{10} bonding interactions at a level of weak hydrogen bonds) may be associated with these short distances. Argentophilicity appears to be a slightly smaller effect than *aurophilicity*, judging by the Ag^+–Ag^+ and Au^+–Au^+ distances in the isostructural compounds $[\mathbf{Ag}(NH_3)_2](ClO_4)$ [4d] and $[\mathbf{Au}(NH_3)_2](ClO_4)$ [6] at the same temperature (170 K): 302.0(2) and 299.0(1) pm, respectively. Much shorter Ag–Ag distances may be seen in constrained systems, of which the dimeric structure of the simple silver acetate is perhaps the most spectacular example, with d(Ag–Ag) = 279.4(4) to 280.9(3) pm [7].

Hg^{2+} as a diagonally related d^{10}-ion forms analogous linear complexes, $[Hg(NH_3)_2]^{2+}$, with Hg–N distances of 207.2(16) pm in $[Hg(NH_3)_2][HgCl_3]_2$ [8], shorter than d(Ag–N) = 212.9(11) to 216.0(12) pm in $[Ag(NH_3)_2](ClO_4)$ [4d] but larger than d(Au–N) = 205.2(2) in $[Au(NH_3)_2](ClO_4)$ [6]. Mercuriphilic effects have not been observed, perhaps due to the higher charge. On the other hand, relativistic effects are, for Hg^{II} as for Au^I, much more pronounced than for Ag^I. One evidence of these effects in mercuric chemistry is the pronounced preference for linear two-coordinate complexes [9], also termed as *characteristic coordination number* (CCN) 2 [10].

As relativistic effects are much less important in silver chemistry, Ag^I exhibits a much larger coordinative flexibility, apparent in coordination numbers between 2 and 6 and in typical closed-shell ion coordination polyhedra (as closed as possible). Other than the hard (Pearson acid) alkali-metal ions, the Ag^+ ion is much more polarizable: thus is a much softer Pearson acid with a higher tendency to coordinate to softer Pearson bases, hence with higher covalent bonding contributions.

In this chapter we report on a number of recently discovered Ag^I complexes with multi-N donor ligands [11] but do not consider this work a comprehensive review. The fact that silver coordination chemistry [12] is presently a rather hot topic may also be seen from a series of leading-edge research papers which have recently been published in the *Australian Journal of Chemistry* [13]. Silver complexes may have a number of functionalities; they may conduct electric current or luminesce, or they may have antimicrobial activity [14], to name only two.

As ammonia (NH_3) is the parent of all N-donor ligands, Ag–N distances as short as, say, 210 pm are considered the landmark for the strongest $Ag^+ \leftarrow N$ interactions ("bonds") possible in $[Ag^I \leftarrow L1]L2$ coordination compounds. L1 is usually a neutral N-donor ligand and L2 is an auxiliary ligand (co-ligand) with a negative charge competing with the L1 ligand for space in the coordination sphere of Ag^+.

1.2 LIGANDS L1 WITH 1,2 N-DONOR FUNCTIONS

1,2-Pyrazole has two directly neighboring nitrogen functions. As competing L2 ligands, triangular (NO_3^-), tetrahedral (BF_4^-, ClO_4^-, SO_4^{2-}), and octahedral anions (PF_6^-) as well as trifluoroacetate ($CF_3COO^- = Tfa^-$) were attempted. In all of these, pyrazole coordinates as a neutral ligand with N2, which bears no hydrogen atom.