

ADVANCES IN **Inorganic Chemistry**
53

Edited by
A.G. SYKES



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Advances in
INORGANIC CHEMISTRY

Including Bioinorganic Studies

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PUBLISHER'S NOTE

The present volume marks the last in the series to be edited by Professor A.G. Sykes FRS in whose capable hands it has been since he took up the position of Editor in 1985 with responsibility for Volume 32. Prior to this, he edited four volumes of the Academic Press series *Advances in Inorganic and Bioinorganic Mechanisms* 1982–1986. The acclaim for the *Advances in Inorganic Chemistry* series and the large number of citations it has received are reflected in the high standards he set and the quality of the authors he was able to enlist to write reviews on topics of interest to inorganic and bioinorganic chemists.

The series began as *Advances in Inorganic Chemistry and Radiochemistry* in 1959, and the first 31 volumes were edited by the Cambridge team of H. Emeléus and A.G. Sharpe. With Vol. 31, the title was changed to *Advances in Inorganic Chemistry*. Professor Sykes extended the area of interest to include Bioinorganic studies. The first three contributors Taube, Fischer and Lipscomb, became Nobel Laureates, and since its inception most leading inorganic chemists have contributed to the series. With an impact factor of 11.5 for the year 2000 – the frequency with which the average article is cited in that particular year (ISI Journal Citation Reports 2000) – the series leads the field of 38 inorganic and nuclear chemistry publications covered.

Professor Sykes has had a long and interesting career since obtaining his PhD at the University of Manchester under the supervision of Professor Bill Higginson in 1958. He spent 20 years at Leeds University before taking up his current post at the University of Newcastle. During this time he has had Visiting Positions in the USA, Germany, Austria, Japan, Kuwait, Australia, Canada, the West Indies, Switzerland, South Africa, Spain, Hong Kong and Denmark. His group has been host to large numbers of post-doctoral fellows and visitors (over 40 different nationalities!), and has produced 53 PhDs. Some 470

publications are attributed to the group. His contribution to the field has recently been honoured in a special volume of *Inorganica Chimica Acta* 331 (2002). The international connections have no doubt been of great benefit in his work as Editor of the series.

We would like to acknowledge the significant contribution of Professor Sykes to the success of the series, and to thank him for all the time and effort he has put in to establish its position as the leading reference work in the field. We wish him all the best for his retirement. At the same time we welcome Professor Rudi van Eldik, from the Institute for Inorganic Chemistry at the University of Erlangen-Nürnberg, who has taken up the Editor's baton. With his research interests in inorganic and bioinorganic mechanisms, Professor van Eldik is the ideal person to develop this series further.

WHEEL-SHAPED POLYOXO AND POLYOXOTHIOMETALATES: FROM THE MOLECULAR LEVEL TO NANOSTRUCTURES

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I. Introduction

The development of new concepts in inorganic chemistry such as host-guest based chemistry, supramolecularity, and the building block approach, together with improvements in structural characterization techniques, has stimulated the discovery and characterization of sophisticated chemical objects ranging from the molecular level (few angströms scale) to extended molecular arrangements (nanometer scale). Most of these compounds are prepared in aqueous solution or in inorganic solvents and are isolated by crystallization or precipitation. Soluble species adapt their size and shape in solution to minimize the

interactions that could provoke their self-aggregation and precipitation but they can also tune their contact surface with the solvent to achieve the ideal entropy value of solvent-interaction. The molecular surface which is most complementary to these two propositions is that of a ring or a wheel. The most beautiful example we know of this is the soluble “big wheel” (see below), one of the key structures to enter mesoscopic coordination chemistry. Some of these wheel-shaped molecules are at the boundary of usual coordination chemistry and nanometric chemistry, and thus will allow us to explore the domain where the macroscopic properties arise from the microscopic level.

This review of the more recent wheels published in the literature covers both the molecular and nanometric domains. Our description will be limited to rings and disks with a minimum nuclearity of 5, the cavity of the wheel being empty or containing something inside, such as ions or templating groups. The review is organized in three parts: (i) rings of 3d-metals in moderate oxidation states (II, III) with O, N, and S-donor ligands; (ii) wheel-shaped polyoxo(thio)metalates containing metals in high oxidation states (IV, V, VI); and (iii) more sophisticated species based on Mo(VI), W(VI), and Mo(V) metal ions located at the boundary of molecular and solid-state chemistry. Not only do some of them have interesting magnetic properties, but in many cases they have been synthesized as “objects of beauty” as Professor Achim Müller first called them.

II. Wheels with 3d Metals in Oxidation States (II, III)

First of all, structures of wheels in which the metals are bridged by more than one atom are precluded from this section. In the latter category, heteroatoms, such as transition metals and nitrogen, substitute methylene carbon atoms in the ring of an organic crown ether and are thus often designated as metallacrown ethers. An example of a 12-metallacrown-4 structure, with four copper atoms bound by 3-amino-N-hydroxypropanamide ligands and an extra Cu atom at the center of the ring (1), is given in Fig. 1. These molecules have been the subject of a recent and extensive review (2).

We will thus consider in this section only metal wheels where the bridges between the $M \cdots M$ vectors are constituted by a single atom, either μ_2 -bridging anions (OH^- , Cl^- , F^- , O^{2-} , S^{2-}) or μ_2 -carbon, oxygen, nitrogen, or sulfur atoms from various organic ligands. The substitution of a transition metal atom for an ethane bridge atom (3) leads to

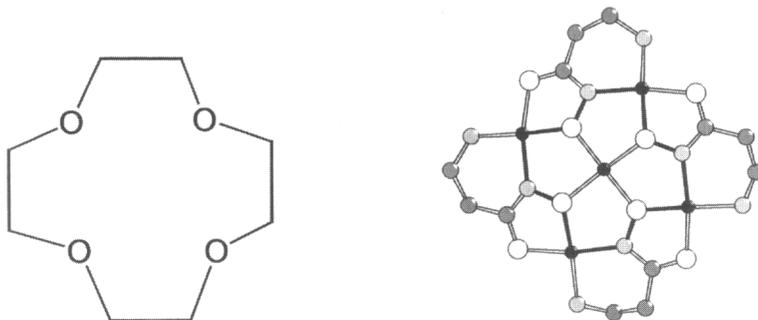


FIG. 1. Schematic diagram of 12-crown-4 (12-C-4) compared with the analogous core of the metallacrown: metal atoms, black spheres; C atoms, light gray spheres; N atoms: medium gray spheres.

a structural analogy with the organic crown ethers, which explains why these metal rings are sometimes also categorized as metallacrowns or metallacoronates. This structural analogy extends to comparable properties for the metallic rings and their organic counterparts. Indeed, like organic crown ethers, the metal wheels can complex small cations, such as alkaline cations or another metal atom, and their syntheses are often rationalized in terms of template effects although they often have been synthesized, by serendipity, from one-pot reactions. Rare examples of metal wheels in supramolecular interaction with anions are also described.

We will make a distinction between the metals with low coordination numbers (2, 4) and those which are surrounded by six ligands, defining an octahedral environment. In the first category, with the exception of the anecdotal mercury compound and the copper complex (see below), the ligands are thiolate or selenate groups; the size of the chalcogenide ion limits the coordination number of the metal to four while, in the second category, a variety of organic ligands is encountered.

A. METALS WITH LOW COORDINATION NUMBERS

The mercury wheel $\{[(\text{CF}_3)_2\text{CHg}]_5\text{Cl}_2\}^{2-}$ is a unique example of a metal ring with μ_2 -C bridging atoms; the cyclic pentanuclear neutral ring $[(\text{CF}_3)_2\text{CHg}]_5$ contains five mercury atoms bridged by one carbon atom of a perfluoroisopropylidene ligand, in a planar ten-membered cycle (Fig. 2) (4). When this metal wheel is mixed with $[\text{PPh}_4]\text{Cl}$, $[\text{PPh}_4]\text{Br}$ or $[\text{PPh}_4]\text{I}$ in ethanol at room temperature, it forms halide complexes (5). In the solid state, two halides are located above and below