

Preface

Gold has a special place in the history of mankind – its chemical inertness and enduring physical qualities make it an ideal metal for the fabrication of high value coins and jewellery. They retain their bright appearance even after exposure to extreme conditions for tens or hundreds of years. Indeed as I write some intrepid gold hunters are seeking to bring up a billion dollars worth of gold bullion from the bottom of the Atlantic. It was originally mined during the Californian gold rush of the 1850s and lost at sea 150 miles East of the Carolinas in 1857 whilst being transported to New York. Colloidal gold has been known since ancient times and was used for making highly coloured glasses. Red and mauve glasses were particularly highly valued by the Romans. The realisation that colloids of the more noble metals could be studied and understood using scientific methods can be traced back to Michael Faraday's research at the Royal Institution in the 1850s. The term colloid was proposed in 1861 by Graham, by which time Faraday had established that gold, silver, copper, platinum, tin, iron, lead, zinc, palladium, aluminium, rhodium, iridium, mercury and arsenic shared the ability to form dilute clear solutions and thin films, which could be detected and studied by their ability to interact with light. This suggested that their dimensions were of the same order of magnitude as the wavelength of light.

In the mid-twentieth century the first examples of structurally characterised molecular cluster compounds of gold were reported by Malatesta and Mason and as a result of research in England and Holland the field was expanded and higher nuclearity examples of these metal–metal bonded compounds were established by crystallographic techniques. These highly coloured compounds were stabilised by tertiaryphosphine ligands, and their relevance to nano-chemistry and colloids was recognised at an early stage. In the twenty-first century the development of a very flexible synthetic route to cluster compounds of gold based on thiolato-ligands provided an important impetus to the field. This coincided with the recognition that gold which has previously been thought to be inferior to the platinum metals as a catalyst for the transformation of organic feedstocks was shown to be active as a homogenous and heterogeneous catalyst. These exciting developments have made it timely to publish a pair of volumes of *Structure and Bonding* devoted to gold clusters, colloids and nano-particles.

The first volume opens with a historical overview of the area and provides not only a broad introduction to the area and defines more clearly the characteristics of gold clusters, colloids and nano-particle. It also addresses their characterisation and their chemical and physical properties. The potential applications of these species are also discussed. Professor Konishi provides a review of recent developments in “Phosphine-coordinated Pure-Gold Clusters: Diverse Geometrical Structures and their Unique Optical Properties”. This area originated in the 1960s, and Professor Konishi has made notable contributions to this area in recent years. This is followed by three chapters by Professors Jin, Chen and Dass, and their co-authors which describe the synthesis of gold clusters based on organothiolato-ligands. An area which blossomed following the report of a widely applicable synthetic method by Brust, Schiffrin and their coworkers in 2006. Although the synthesis of these compounds is relatively straightforward the methods result in mixtures of cluster compounds and these chapters discuss the techniques which have been developed in order to produce mixtures which either contain fewer components or are amenable to modern separation techniques. The development of more sophisticated purification techniques has led to single crystals of many of these clusters which have been structurally characterised to atomic resolutions. These structures have revealed some novel architectures and also led to the important realisation that in these clusters the gold atoms have a dual role. They not only contribute to the central core, but also contribute novel gold-thiolato-ligands, which protect the surface of the cluster. Professor Schmid, who was an important contributor to the original development of the syntheses of high nuclearity gold clusters, has written with Professor Simon and Dr. Broda a chapter on the “Size and Ligand Specific Bioresponse of Gold Clusters and Nanoparticles”. They emphasise new research which suggests that the high nuclearity gold phosphine clusters have important applications in the areas of biochemistry and medicine. These chapters generally deal with the synthesis of clusters prepared in water or organic solvents and the balance is restored by an important chapter by Professor Fielicke and Dr. Woodham which discusses the synthesis and properties of gold clusters in the gas phase.

The second volume starts with historically based account of the bonding in gold clusters. In the late twentieth century empirical molecular orbital calculations provided some important insights into the bonding in these clusters and led to the development of bonding models which were sufficiently robust to predict the structures of specific clusters and provide a broad framework for understanding the structures and reactions of molecular cluster compounds. The great increase in computer power since that time has made it possible to apply *ab initio* molecular orbital calculations to large gold clusters and the results have provided important insights into the bonding interactions which are responsible for their stabilities and structures. The relevance of DFT calculations is emphasised in the chapter by Professors Johnston and Li on gold nano-alloys and clusters. The importance of gold clusters in catalysis is stressed in the chapter by Professor Freund and his co-authors titled “Model Catalysts Based on Au Clusters and Nano Particles”. The final chapter by Professor O’Hair and his co-authors underlines the importance of

mass-spectrometry in the characterisation of gold clusters in their chapter titled “Gas Phase Formation, Structure and Reactivity of Gold Cluster Ions”.

This is an exciting and rapidly developing area of nano-science and is attracting chemists, physicists and material scientists. The resulting interdisciplinary research continues to throw up many interesting structures and applications. I thank all the authors and the editorial staff at Springer for contributing to a volume which helps to define the field for those who are outside it and the stimulation to those in the field to make it one of the important areas of science in this century.

Oxford, UK
May 2014

Michael Mingos

Gold Clusters, Colloids and Nanoparticles II

Mingos, D.M.P. (Ed.)

2014, IX, 233 p. 110 illus., 68 illus. in color., Hardcover

ISBN: 978-3-319-07844-1