

Silver Coordination Polymers — From Simple Complexes to Functional Networks

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There is current world-wide interest in functional materials and many ‘molecular’ chemists are redefining themselves as ‘materials’ chemists. One of the core areas of activity relates to hybrid organic–inorganic materials with coordination bonds between the metal centre and ligand donor atoms providing the assembly motif. By appropriate ligand design and judicious choice of metal centre, it is possible to exert significant control over the course of the reaction and to have reasonable expectations of preparing materials of defined and anticipated dimensionality. These materials are often known as coordination polymers, and metal–ligand interactions join with hydrogen-bonding, polar and dipolar, and aromatic–aromatic interactions in the arsenal of the modern crystal engineer.^[1] Many of the pioneering studies in the systematic design and study of coordination polymers originated in the Robson group and the legacy of this work is seen today in the concepts of crystal engineering.^[2] It is, therefore, especially appropriate that a Research Front on silver coordination polymers should be published in the *Australian Journal of Chemistry*.

Although the study of coordination polymers is a relatively young field, the methodology is mature and is based firmly on the concepts of coordination and metallosupramolecular chemistry.^[3] In general, the coordination properties of the metal ion (coordination number and geometry) are matched to the donor properties of the ligands and the interplay of the two defines the properties (discrete polygons or polyhedra, one-, two-, or three-dimensional coordination networks) of the organic–inorganic construct. This Research Front is concerned with the use of silver(I) ions for the assembly of coordination polymers and the timely review by Su^[4] serves to emphasize and quantify the increasingly important utilization of this element in crystal engineering. Why is this?

What are the unique features of silver that have resulted in this resurgence in silver coordination chemistry — for this is a true rebirth and re-invigoration of interest in an element that was previously regarded as possessing a rather staid and uninteresting coordination behaviour. The papers in this Research Front address many of the key features of silver-containing coordination polymers — variable coordination numbers and geometries, combinations of metal–ligand and other supramolecular interactions, silver–silver interactions, and photophysical, electronic, and biomedical applications.

The coordination chemistry of silver is both fascinating and frustrating... it is perilous to attempt to assign a preferred coordination number or ionic radius to silver(I) as it tends to exhibit a continuum of metal–ligand distances which vary from ‘bonds’ through ‘interactions’ to ‘non-bonded interactions’. In the papers in this issue, three-dimensional structures are determined by additional weak interactions involving silver–donor atom,^[5] silver–hydrogen,^[6] or silver–silver^[7] interactions. The interplay of all of these interactions is seen in the contribution from Janiak and Fromm in which the observed solid state structure has numerous subtle interactions dictating the network that is formed.^[8] Even when the coordination number is well defined, the coordination geometry is not necessarily predictable.^[9] A d^{10} metal ion is expected to have a coordination geometry dominated by steric factors. The use of metal centres with variable coordination geometries and coordination numbers, or indeed with no strong preference for any particular geometry, contrasts with the usual approaches to metallosupramolecular chemistry and allows for less precisely optimized ligands to be used. This is effectively utilizing fuzzy logic for processing the metal–ligand interaction data by allowing partial set membership



Ed Constable was born in Edinburgh. His initial training took place at the Oxford University (B.A. chemistry 1978; D.Phil. 1990) which led to a love affair with ruthenium chemistry and photochemistry that continues to this day. He held a number of research fellowships at Cambridge University before being appointed to a University Lectureship and Fellowship in 1984. He remained at Cambridge until 1993 when he accepted an appointment at University of Basel. In 2000 he left Basel for the University of Birmingham, but returned to Basel in 2002 to take his current position of Professor of Chemistry in 2002.

(different coordination numbers and geometries) rather than crisp set membership or non-membership.^[10]

What are the challenges for the future? No good algorithms or predictive methods are available for predicting the outcome of silver(I) coordination events. Very few studies are made of the solution speciation in solutions of, and in the mother liquors above, the coordination polymers. With chiral ligands it is sometimes, but not always, possible to obtain unidirectional or handed coordination networks.^[11] Is it possible to control the balance of supramolecular interactions to engineer the directionality? Anyone who works with silver(I) chemistry will have experienced the formation of short silver–silver contacts and the phenomenon of argentophilicity,^[12] but can it be used in a controlled manner to give predictable solid state effects?

Whatever the success in understanding and quantifying the effects, there is no doubt at all that silver coordination polymers will continue to surprise and entertain us with their structures and hopefully bring the promised functional properties to fruition in the near future. In the meantime, enjoy the discovery of the structural diversity associated with the silver chemistry presented in this Research Front.

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