The Concept of Coordination

Foreword

The concepts of a living science such as chemistry are necessarily in a state of flux. It must then be asked how precise a definition may be attached to an expression such as 'The Concept of Coordination', to which our reply is that at best a definition can be given that was popularly accepted for a certain period of time and that our objective in compiling this edition of *C. R. Chimie* was to present an overview of how the concept may have changed with time and of some of the forces that may have shaped this change. This proved to be an exceedingly ambitious project and within the scope of a single edition of the journal, it is hardly possible to do justice to the stupendous range of human activity that could be encompassed, though fortunately there are earlier assessments of the relevant chemistry that have been more generous in this regard [1]. We consider, nonetheless, that an essential aspect of communication in science is an examination of the language used in that communication and that even the most incomplete or contentious of analyses can be of value in provoking an assessment of more sober others.

What, then, may be meant by the term *coordination*? This is not necessarily the same as defining the *concept of coordination*, but is perhaps a step towards it. It is possible to answer the question by pursuing an historical pathway, but this would perhaps be even more convoluted than to offer a contemporary definition (as follows) and analyse its fit to changes in the perceived meaning of *coordination* that have occurred over the past century. Thus, a very simple interpretation of the statement that atom A is *coordinated* by atom B might be merely that the Cartesian coordinates of the two atoms are similar. This requires that the term *similar* be explained, and one possible explanation is that it means that the coordinates are such that the measured distance between the two atoms may range from ~0.9–4 Å, depending upon the particular atoms involved. This is no more than an alternative naming of conventional 'bonding' separations, except in that it involves no mention of the factors that may lead to two atoms being in such a degree of proximity. Thus, it leads to no immediate distinction between *coordinate* and any other form of bonding (leaving aside the issue of whether there is any point to such distinctions). In addition, it makes no mention of the rate at which the distance between any pair of atoms may change with time, an issue that can become important when both kinetically labile and inert systems must be considered. It is also a deceptively simple definition, since diatomic species are not the most abundant of chemical entities and allowance for the possibility that one atom – the 'central' atom – may be coordinated by more than one other leads to a variety of complications. One is that even when the atoms that surround the central atom and are thus said to be coordinated to it are all the same, they need not be at identical distances from that central atom. A related complication is that, at least in condensed phases, interatomic distances fall into various ranges, with that of 0.9–4 Å simply designating closest approaches, thus leading to the notion that the environment of any atom may be defined in terms of primary, secondary, etc. *coordination spheres*. In these terms, the first complication mentioned above becomes one of deciding to which coordination sphere an atom should be assigned. As exemplified in recent discussions of whether the cation present in aqueous solutions of copper(II) compounds should be regarded as $[Cu(OH_2)_6]^{2+}$, $[Cu(OH_2)_5]^{2+}$ or $[Cu(OH_2)_4]^{2+}$ [2], this is not necessarily a trivial task! In these formulae, of course, the square brackets have a rather special meaning, often loosely interpreted as meaning that they enclose and thus define a central atom and its primary coordination sphere in a *coordination complex* (with the overall charge, considered to be largely localised on this aggregate, shown

outside the final bracket), since not all the atoms, here, the hydrogens, would strictly be considered to be within the primary coordination sphere. (Thus, the *coordination number* equals simply the number of oxygen atoms.) They are formulae that reflect other aspects of the development of a model of coordination, those associated with analysis of the chemical bonding involved, so that another interpretation is that the square brackets enclose a Lewis acid (here, Cu(II)) and all the molecules – ligands – containing a Lewis-base centre (here, O) or *donor atom* involved in the formation of a *coordinate bond* to the central atom. This is a simple and familiar interpretation, though also one with various inadequacies, as illustrated, for example, by the development in the Chatt–Dewar–Duncanson model of alkene coordination to metals in which all centres have both Lewis acid and Lewis base characteristics. Interestingly, application of this model to the paradigmatic system of 'Zeise's salt', $[PtCl_3(C_2H_4)]^-$, raises the question of whether the coordination number should be related to the number of adjacent atoms or the number of electron pairs supposedly involved in donation, a dilemma that also arises in considering some complexes formed by small-ring chelate ligands such as nitrate. Overriding any of these issues is that of whether a formula showing a central atom and its primary coordination sphere is an adequate representation of the species actually present, a question which is of fundamental importance for improving precision in the communication of chemical observations from one individual to another. Relative to the energies of interaction of closest pairs of atoms – conventional bond energies –, the energy required to turn a reaction rate or equilibrium to a useful extent in a desired direction is small, so that interactions that might be considered, a priori, weak cannot generally be neglected, one of the reasons why control of chemistry is not simple! Certainly there is extensive evidence that well-defined secondary coordination spheres exist and that changes in their structure can dramatically alter properties considered to be associated with the central atom or indeed, in a further extension of the notion of coordination, with some central cluster of atoms.

Thus, a definition of the 'concept of coordination' is that it is the idea that the behaviour of a chemical entity depends upon its environment, both near and far. In this general sense, it is closely allied to the concept of a *supermolecule* and the features of its structure which determine its properties [3]. In practice, the term *coordination chemistry* continues to be used in a restricted sense as one to describe the chemistry of metal-containing compounds (*coordination complexes*), though the fact that coordination chemistry includes the field of *reactions of coordinated ligands* shows that it does encompass the study of the influence of the environment on non-metal centres. There may, of course, be some utility in maintaining even an artificial distinction between coordination and supramolecular chemistry in that different perspectives may assist in the development of an understanding of sophisticated systems, but it is unclear how long such a benefit might last.

Of the experimental techniques that provide a stimulus to the evolution of concepts such as that of coordination, none is more important than X-ray crystallography. In recent decades, technical improvements in crystallographic equipment have resulted in an extraordinary upsurge in available structural data, consequently providing new challenges for bonding theory and for the symbolic representation of the materials studied. A remarkable recent example of a structure determination for a coordination complex is that of $[AuXe_4][Sb_2F_{11}]_2$ [4], where the 'inert' gas Xe is coordinated to Au formally in the unusual oxidation state of +II. Much longer-known gold complexes such as $[N\{AuP(C_6H_5)_3\}_5]^{2+}$ and $[C\{AuP(C_6H_5)_3\}_6]^{2+}$ [5] have also posed interesting problems for bonding theory, though the 'unusually' high coordination numbers for N and C in these compounds are really not so unusual in the general context of organometallic and bioinorganic chemistry. Other derivatives of heavy metals, some of those of U, Pb, Hg and the lanthanides providing examples in the present articles, are frequently found to have coordination environments that are difficult to describe because of the wide range of interatomic distances to atoms surrounding the metal and because of their irregular stereochemistry.

Crystallography is particularly useful in defining atom approaches for compounds that are labile in solution, a recent instance being in the definition of alkali-metal-ion interactions with aromatic pi-systems, a type of interaction long known for kinetically inert transition-metal compounds such as ferrocene. Hydrogen is another element commonly involved in labile interactions and crystallography has been crucial in establishing situations where it has a coordination number of

2 or more, one instance of this being in the definition of 'agostic' interactions. Much more familiar is the situation described as *hydrogen-bonding*, though it is interesting, given the very common use of the example of protonation of ammonia as an introductory example of the formation of a coordinate (or 'dative') bond, that only recently has the ammonium ion coordinated by four ammonia molecules (through hydrogen bonding) been fully structurally characterised as an entity present in $[NH_4(NH_3)_4][B(C_6H_5)_4]\cdot NH_3$ [6]. This structure also provides evidence for $NH\cdots\pi$ interactions and offset face-to-face interactions involving the anion phenyl rings, and its analysis raises some possibly very significant questions as to the meaning of comparing observed interatomic distances with van der Waals radii sums.

Alfred Werner, the 'father of coordination chemistry' [1], did not discuss and could not have discussed, given the physical techniques available to him, the nature of coordination complexes in terms such as those used above. Given only a knowledge of stoichiometry and a nineteenth-century concept of 'valency' as involving interaction between adjacent atom pairs, he was nonetheless led to definitions of 'primary' and 'secondary' valencies akin to much later definitions of 'oxidation state' and 'coordination number', respectively, and quite consistent with the still later idea of multiple coordination spheres. Of course, one of the benefits of hindsight is that it brings out clearly the important role of good fortune in research. Influential ideas have often been the fruit of rather particular circumstances or even imperfectly understood experiments, an example being provided in Alfred Werner's fortunate choices of ethylenediamine (ethane-1,2-diamine) as a ligand that would occupy two coordination sites about a single metal and of cobalt as the metal on which most of his investigations were based.

Most of the issues referred to above are explored to some extent in the various articles which follow. Some broader issues, such as the confusion that may arise when kinetic and thermodynamic aspects of a system are not explicitly distinguished [7] and the very difficult task of defining a clear and concise nomenclature, no doubt deserve more attention, so we can only hope that the present discussion will serve as a stimulus for such extension.

References

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Jack M. Harrowfield *
George Koutsantonis
Chemistry, School of biomedical and chemical sciences, University of western Australia, 35 Stirling Highway, Crawley, WA 6009, Australia
E-mail address:
harrowfield@isis.u-strasbg.fr (J.M. Harrowfield).

Available online 11 January 2005

* Present address: Laboratoire de chimie supramoléculaire, Institut de science et d'ingénierie supramoléculaires (ISIS), 8, allée Gaspard-Monge, 67083 Strasbourg, France