

**Sidney F.A. KETTLE**  
*University of East Anglia, School of Chemical Sciences*

## STRUCTURE IN INORGANIC CHEMISTRY

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**ABSTRACT:** The word 'structure' in inorganic chemistry has proved to be rather elastic. Some aspects of this elasticity are reviewed. In the future, it is likely to continue this pattern, perhaps to the extent that the subject of inorganic chemistry becomes itself less identifiable. [*Chem. Educ. Res. Pract. Eur.*: 2001, 2, 105-107]

**KEYWORDS:** *inorganic chemistry; electronic structure; molecular structure; subject structure*

### INTRODUCTION

One of the features which has characterised chemistry over the years has been the way that its central concepts have proved to be rather elastic; to some a joy but to others, sometimes, a source of irritation. It is not much fun to discover that the subject has changed behind your back! Inorganic chemistry has been very much part of such developments. John Dalton would scarcely recognise the atom concept of today, with its orbitals, contour diagrams and mathematical descriptions. Equally, the concept of the chemical bond has changed. Once, it was a topic with sub-divisions such as polar, covalent, ionic, dative and semi-polar. Then labels such as single, double, triple, delocalised, hybrid, sigma, pi and electron-deficient were added. Now, the concept has assumed a new fluidity in which it is often difficult to talk about a designated electron pair interaction as being uniquely bonding, non-bonding or antibonding, ionic or covalent. Strange animals such as relativistic contributions and density functionals have made an appearance<sup>1</sup>.

### STRUCTURE, PAST AND PRESENT

In this mobile world it is not to be expected that the concept of structure has remained immune to change. When Werner synthesised cobalt complexes the work was in large measure driven by a desire to establish their structure (and the 'secondary valence' of cobalt)<sup>2</sup>. 'Structure' here was a determination of the gross geometrical characteristics. The 'structure determination' of the crystallographers that were to come represented something much more precise, although the Werner interpretation lived on in the work of many vibrational spectroscopists (although, to be fair, they did their best to move towards a more detailed description through things like Badger's rule<sup>3</sup>). Then the meaning of 'structure' began to include 'electronic structure' and we were back, in part, to chemical bonding revisited, although the important part played by models that invoked no bonding - the Valence Shell Electron Pair Repulsion model in particular - must

not be overlooked<sup>4</sup>.

Today, molecular structure in the sense of the geometrical arrangement of atoms in molecules and extended lattices, is much less of a concern, although it remains of interest and surprises still occur. Crystal structure determinations are routine in the majority of cases and NMR methods are often successful for those cases where crystals cannot be obtained (although not as routine as crystallographic methods). Structure in terms of synthesis remains as active an area as ever. The focus seems to have moved from transition metals, *per se*, towards main group elements where the synthesis of novel ring and chain species, including dendrimers, is showing continued activity. Structure mimicry is a very active area, where the aim is usually that of creating relatively easily synthesised analogues of biologically important species. The long-term implications for catalysis are enormous - and could well lead to a change in the structure of parts of the chemical industry. Imagine the consequences of the replacement of the Haber process, for instance. Creation of new solid materials with catalytic potential is an area in which new structures are being developed with increasing rapidity; many can be thought of as derived, conceptually if not chemically, from zeolitic materials. Finally, and also far from trivial, are attempts to produce molecular equivalents of semiconductor and magnetic devices. Molecular wires, molecular diodes, molecular switches, molecular memories and molecular transistors are structures which are actively being sought<sup>5</sup>. And what of the electronic structure of these new creations, and, indeed, of old ones? Much could be said. For the heavy elements, for sure, it has become clear that relativistic effects cannot be ignored. So, it now seems clear that the major qualitative differences between the chemistries of silver and gold lies in the importance of relativistic effects in the latter; they also explain why mercury is a liquid<sup>6</sup>. Whilst the usefulness of crystal and ligand field theories in teaching remain, it is now clear that they must not be applied outside their local context. So, seems that it commonly happens that, although the d-shell remains unfilled, there are filled ligand orbitals at higher energy<sup>7</sup>! Even more confusing are the new theoretical methods which seem capable of giving results of chemical accuracy (and that means of chemical relevance) for even fairly large inorganic molecules containing heavy atoms. In part, they do so by being, or trying to be, many-electron methods - and this means that a one-electron interpretation (and so in terms of orbitals of some sort or another) of the results is not too easy<sup>7</sup>.

### HAS STRUCTURE A FUTURE OR THE FUTURE A STRUCTURE?

And what of the future? It needs more than a crystal ball. In the immediate future, for sure, the present trends will continue - but that takes no great insight. If I had to make a prediction of a major change into the future it would be in terms of excited states. Traditionally, we think of the chemistry of an element or, at least, of that of a particular compound. In fact, each and every molecule has a number of chemistries. In a given electronically excited state, the bond angles and bond lengths differ to some extent from those of the ground state with which we are familiar. The chemistry differs too, and it is here that there is much to discover. Of course, these differences are meaningless unless we have some way of studying them. Two things are needed. An ability to generate specific excited states and then an ability to study them. Recent advances in ultra-short laser pulse generation and of multi-laser excitations bring these abilities much closer<sup>8</sup>. Of course, most of the study, at least initially, will involve gas phase work - but this, in turn, will help us better to understand the influence of the solvent in ordinary commonplace chemical reactions. At the moment, theoretical insight the electronic structure of excited state molecules is not great, particularly when unpaired electrons are involved.

But, do I hear you ask - is this inorganic chemistry? There was a time when, at least informally, inorganic chemistry was defined as chemistry done by inorganic chemists. That is,

anyone who felt themselves to be an inorganic chemist, by definition, did inorganic chemistry. In my observation, times have changed and a much more synthesis-based definition now operates (you can check by observing how the content of established inorganic chemistry Journals has changed over the last quarter of a century - Inorganic Chemistry seems to me to be a notable exception). Perhaps future changes will be even greater. I have in front of me the year 2000 Christmas letter from a well-known Chemistry Department, Northwestern, in Evanston. I quote:-

.. our view that within the next few years this Department will no longer be divided among the traditional sub-fields of inorganic, organic and physical chemistry but rather will be concerned with the Chemistry of Life Processes, Materials Chemistry, Catalytic Chemistry and Environmental Chemistry.

If this is right, the biggest structural change to come is not one discussed in this article!

**CORRESPONDENCE TO:** *Sidney F.A. KETTLE, School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ, England; e-mail: S.Kettle@uea.ac.uk*

**Sidney F.A. Kettle** is a Professorial Fellow in the *School of Chemical Sciences* of the *University of East Anglia (UEA)*. He has published over 200 papers, mostly on spectroscopy and related areas. He is currently Editor of *Spectrochimica Acta A*. He is the author of (1) '*Valency Theory*' (with John Murrell and John Tedder), (2) '*The Chemical Bond*' with the same co-authors, (3) '*Coordination Compounds*', (4) '*Symmetry and Structure*', and (5) '*Physical Inorganic Chemistry*'. He has also published numerous articles in the *Journal of Chemical Education*, mainly on group theory and its applications to chemistry, and has been involved in staff development work in many countries.

## NOTES AND REFERENCES

<sup>1</sup> For an overview, see S.F.A. Kettle, '*Physical inorganic chemistry*', OUP, England, 1998.

<sup>2</sup> A Werner (trans. by E.P. Hedley) '*New Ideas on Inorganic Chemistry*' Longmans, Green and Co., London, 1911.

<sup>3</sup> R.M. Badger, *J. Chem. Phys.*, 1934, 2, 128; R.M. Badger, *J. Chem. Phys.*, 1935, 3, 710.

<sup>4</sup> For a brief account see F.A. Cotton and G. Wilkinson '*Inorganic chemistry*' 5th Edn., Wiley, New York 1988. It is interesting, and perhaps significant, to note that this topic does not appear in the 6th Edition of this book.

<sup>5</sup> A brief, but contemporary, overview is given in '*Taking baby steps to 'moletronics''*' by R. Dagani, *Chem and Eng. News*, Jan 3, 2000, p22.

<sup>6</sup> L.J. Norrby, *J. Chem. Educ.* 1991, 68, 110

<sup>7</sup> See '*Computational Transition Metal Chemistry*' *Chem. Rev.* 2000, 1000, 351-818.

<sup>8</sup> A.H. Zewail, '*Femtochemistry: atomic-Scale Dynamics of the Chemical Bond Using Ultrafast Lasers (Nobel Lecture)*' *Angew. Chem. Int. Ed.*, 2000, 39, 2587.