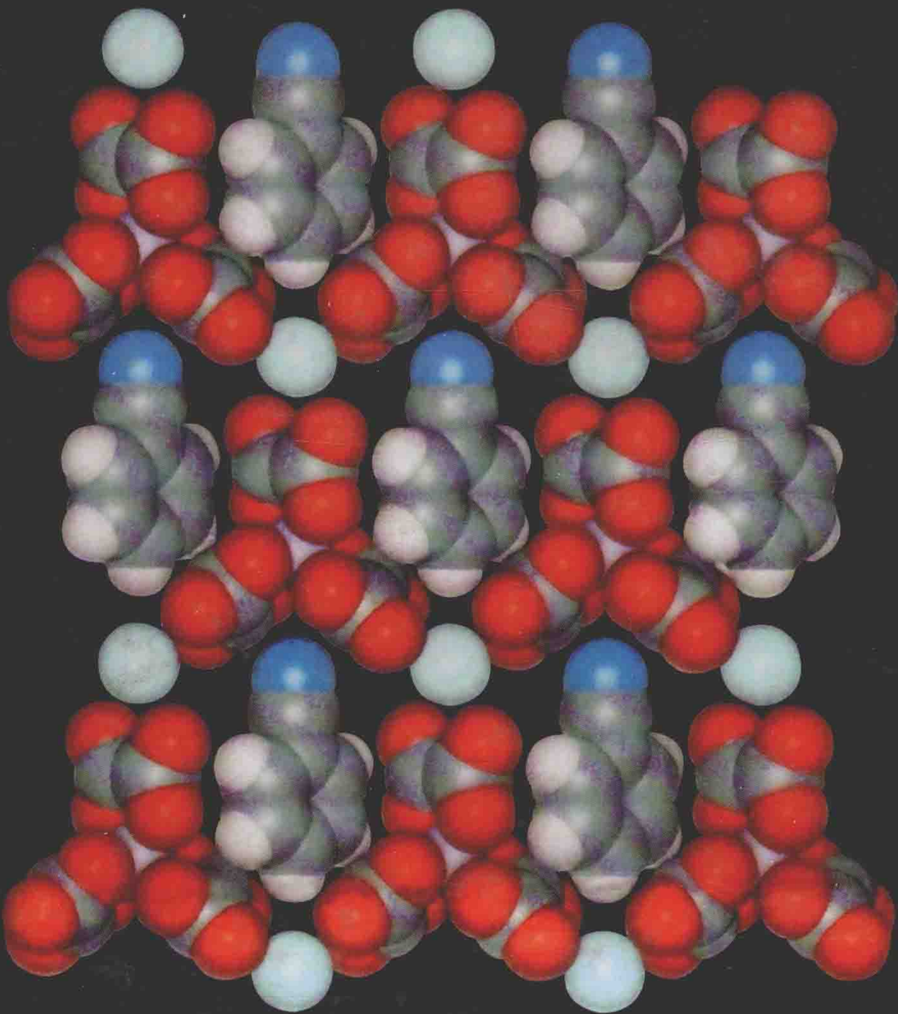

MOLECULES INTO MATERIALS

Case Studies in Materials Chemistry —
Mixed Valency, Magnetism and Superconductivity

PETER DAY

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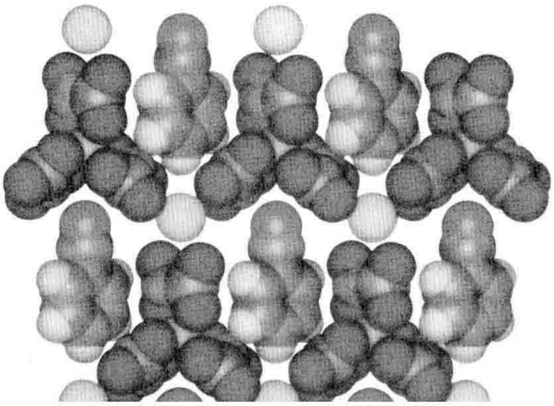

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MOLECULES INTO MATERIALS

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Dedication

The articles collected together in this book represent the accumulated efforts of a very large number of people over the years such as final year undergraduate project students, graduate students, postdoctoral research assistants, Research Fellows, exchange visitors from many countries, and colleagues from many University Departments and Research Institutes. I hope I can bring them all together under the common heading '*friends*'. The results described in these pages are largely due to their skills and insights. Unfortunately, there are too many to name individually and to single out names would be invidious. So this book is warmly dedicated collectively to my ***co-workers***.

Why this book?

Science, as much as politics, is concerned with issues. At each moment, as the clock moves forward, communities with common interests and enthusiasts for particular doctrines or approaches (activists, in political parlance) turn their searchlights on to matters that appear to be of importance at that instant. However, there is a profound difference between science and politics in this regard. In politics, the big issues (personal freedom, collective action) keep recurring in different forms; in science, each field, once ploughed, never reverts entirely to scrub; the understanding gained is added to the pile, often to be deployed later in different circumstances. It is in that spirit that the present book is conceived. It collects first (or very early) thoughts on several topics that have since gained wider prominence and interest. Science being an experimental business, many of the articles reproduced here contain data or procedures that may have been superceded in the following years or decades; even the compounds themselves are often only the simplest prototypes, known as 'proofs of principle' by the patent attornies. Nevertheless, it is hoped that their interest is not just historical or even archaeological, but that it will offer some sense of science in formation.

The core matter of this body of work can be subsumed under the label 'materials chemistry', a phrase that was entirely unknown at the time this work began. It is certainly Chemistry since it deals with the way that atoms are brought together to form molecules or more extended arrays, and the properties that flow from that. The properties, however, are largely physical ones and may be classed as electronic, i.e. spectroscopic, magnetic, electron transport and the like. Not only electronic, but collective (i.e. belonging to the ensemble as a whole rather than one individual constituent unit) and this is what constituted the traditional boundary between chemistry and condensed matter physics at least in the 1960s and 1970s. That was the era when physicists began to realise that there were many fascinating collective phenomena to be observed in solids that contained many more than two atoms in a unit-cell and chemists to appreciate that there was a wide world of possibility beyond the individual molecule. It was a privilege for me to play some part in bringing about this evolution, but in summing up the transformation that has taken place in solid state science over the past 40 years, let me defer to the words of a theoretical physicist. Great excitement accompanied the discovery of the first organic molecular superconductor in 1980 [1], but at a gathering of chemists and physicists discussing the new horizons being opened up even in advance of that date, Bill Little (exponent of excitonic superconductivity — still yet to be observed) made the following prophetic remarks:

... The quest for a truly organic superconductor remains a major goal of many research efforts. In a very real sense this is what keeps much of our research afloat. A fortunate by-product has been the large amount of exciting physics and chemistry which has resulted from these endeavours. This has more than justified the effort to date. But perhaps the most valuable consequence and one which will have greatest long term impact has been the emergence of research groups where true interdisciplinary work is done, where physicists and chemists have learned to talk and work with one another in close effective collaboration. The impact of this on materials science can be expected to be great [2].

His words were now proven right.

For an inorganic chemist, the journey from molecules to materials starts with coordination chemistry, one of the ways in which metal ions, that have so many fascinating properties like magnetism or optical spectra, enter into the molecular state. My story begins from a desire to rationalise the optical spectra of molecular transition metal complexes involving the transfer of electronic charge from one part of the molecule to another. That triggers a host of phenomena (first remarked a century ago because they were visually spectacular) which arise from the way the molecular coordination complexes interact with one another when placed side by side in a crystal. These range from shifts in absorption bands that arise from intramolecular excitations to the ones where an electron is transferred from molecule to molecule. In the latter case (mixed valence), it proved possible to rationalise properties of such compounds across the Periodic Table through a simple model that has stood the test of time for 40 years.

Finally, we come to extended interactions across the entire crystal lattice, well known in continuous lattice compounds such as oxides, but much less appreciated in molecular inorganic compounds. Here, not only magnetism but also extreme quantum mechanical effects like superconductivity come into play. For example, the interplay between magnetism and superconductivity becomes an arena for molecular chemists, and at the same time gives rise to complications such as structural chirality.

None of this complexity was dreamt of either by physicists or chemists in the 1970s. This collection of reprints endeavours to chart at least one trajectory of progress through the ensuing jungle. It could never have been accomplished without the enthusiastic and talented support of many students and collaborators (for that word read 'friends'), whose names appear among the publications' co-authors. To them, my gratitude is immeasurable and hence as a small token of thanks, I dedicated this collection to them.

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