

## OBITUARY

# Frank Albert Cotton (1930–2007)

Inorganic chemist, educator and discoverer of the quadruple bond.

Among the greatest thrills for a scientist are those that occur at the moment of discovery. For a chemist, discovery is often synonymous with the creation of a new molecule in the laboratory. But understanding can be an even higher calling: the ability to recognize and explain properties of matter that others have previously encountered but could not comprehend. From understanding, one can derive new principles with which to interpret, or even predict, future results. Few individuals have contributed as much to inorganic chemistry through both discovery and understanding as Frank Albert Cotton. His death on 20 February, at the age of 76, marks the end of an extraordinary and prolific career.

The signature discovery to emerge from Cotton's laboratory at the Massachusetts Institute of Technology (MIT) came in the early 1960s. This was a time of renaissance in coordination chemistry — the study of metal-ligand complexes — and it was fuelled by the rediscovery of a theoretical model known as crystal field theory. Cotton and his colleagues applied this theory in their search for transition-metal complexes with unusual spin states and magnetic properties. They obtained rhenium compounds of relatively low oxidation state in which the distances between adjacent metal atoms were shorter than in the bulk metal itself.

The geometry of the simple  $[Re_2Cl_8]^{2-}$  ion was especially noteworthy. In this ion, an extremely short metal–metal bond of just 2.27 Å linked two  $\{ReCl_4\}$  fragments, with no additional bridging ligand. Moreover, the two halves of the dimer were in an ‘eclipsed’ configuration, with the chlorine atoms on either side swept back to a separation of about 3.5 Å to avoid non-bonded repulsions between them. For some reason, the unit adopted this geometry rather than avoiding such a steric clash by rotating one half of the dimer by 45°.

Cotton quickly understood the importance of this result. It meant that there was a quadruple bond in the  $[Re_2Cl_8]^{2-}$  ion, the first to be identified. In addition to one  $\sigma$  and two  $\pi$  bonds between the rhenium atoms, as occurs in the triple bond between two nitrogen atoms in the  $N \equiv N$  molecule, there was an additional linkage, known as a  $\delta$  bond. Formation of this bond required the chlorine atoms to adopt the eclipsed geometry.

Like all ground-breaking ideas in science, the consequences of this insight were profound. The finding that chemical compounds could have such multiply bonded metal–metal units launched a whole branch

of inorganic chemistry and, later, materials science that kept Cotton's laboratory and others across the world occupied in the ensuing decades. Both experimentalists and theorists recognized the importance of this rich new vein of chemistry.

An essential tool in the structural characterization of metal–metal-bonded compounds was X-ray crystallography. Cotton applied this technique so prodigiously, and advocated its more general use in structure determination so effectively, that it became a routine tool for investigating any chemical substance for which suitable single crystals could be obtained. With remarkable energy and creativity, the Cotton laboratory turned out a stunning display of compounds with double, triple and quadruple metal–metal bonds spanning many of the elements of the transition-metal series. By counting electrons, one could predict the character of many of these new creations — a remarkable achievement.

But Cotton's contributions were not limited to these metal-cluster compounds. In a series of imaginative studies, he and his colleagues prepared and investigated the physical and chemical properties of organometallic complexes. Many of these compounds contained carbon–carbon double bonds that were linked to one or more transition-metal ions. To clarify their structures, Cotton invented the ‘hapto’ or  $\eta$  nomenclature now used to indicate the number of carbon atoms bonded to a given metal atom.

Using nuclear magnetic resonance spectroscopy, typically applied to solutions of compounds over a temperature range, Cotton and his co-workers mapped out the relative motions of ‘fluxional’ organometallics, in which metal ions and organic fragments are involved in an elaborate intramolecular dance. They thus created fascinating motion pictures of movements within these complexes, and their studies were soon followed up by many laboratories. If a scientist's achievements can be measured by his or her ability to inspire

the work of others, Cotton ranks with the very best twentieth-century chemists.

Al Cotton was a champion of fundamental research. His passions were learning, uncovering the secrets of nature and creating new molecules. As an adviser to the US government while a member of the National Science Board, and in other arenas, he championed the cause of funding basic research that is driven purely by intellectual curiosity, rather than by the latest fads in applying chemistry to its many sister disciplines in the

life sciences and in engineering.

Cotton was also an extraordinary educator, writing textbooks at levels ranging from high school to advanced graduate, on topics from elementary and advanced inorganic chemistry to the application of group theory. These texts have been translated into many languages, and in total have sold more than a million copies. At MIT, and subsequently at Texas A&M University, he mentored well over 100 PhD students, and his laboratory was a popular training-ground for numerous postdocs and sabbatical visitors representing 30 countries.

Al took a deep personal interest in his postdoctoral and PhD students. I myself recall his wise advice about my future career choices when, as I was nearing the end of my graduate days in his lab at MIT, we were riding on horseback one beautiful autumn day near his home southwest of Boston. At that moment, and at many others spanning more than four decades, I was the beneficiary of his counsel and support, as were many others. His life in itself was an inspiration that taught the benefits and joys that reward hard work, deep thinking and the search for unexplored frontiers.

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