The Enigmatic Cipher, and Stoichiometry into Stereochemistry – H. M. Powell's Early Contributions to the Study of Chemical Bonding and Molecular Complexes★

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Having been brought up in a world in which chemical bonding and intermolecular interactions are for most purposes distinguished, and are largely understood, most of us find it difficult to realise how recently these concepts have been separated and their structural implications classified. H. M. Powell, in the first issue of this *Journal* [1], has described his early concern to investigate the significance of the dot – the enigmatic cipher used to hide ignorance of the type of attachment of solvent of crystallisation and other molecules in such chemical formulae as $Ni(CN)_2 \cdot NH_3 \cdot C_6H_6$ and $3C_6H_4(OH)_2 \cdot SO_2$. He describes how he became interested, as an undergraduate, in the *cis* and *trans* forms of tetramethyl ferrocyanide and the fact that they usually crystallise as solvates, by reading of their preparation for use in osmotic pressure experiments. He mentions that he was able to distinguish between the two forms by methods of optical crystallography, before X-rays were available to him. Later [2], he was able to confirm that they were indeed *cis* and *trans* isomers, by X-ray structure determination. So started two of his major research interests – the constitution of cyanides and related compounds, and the nature of solvates and molecular complexes (the quest for the cipher's meaning).

His first paper [3] concerned another substance, lead monoxide, that was capable of existing in more than one form. In addition to the two known (yellow and red) polymorphic forms, Applebey (Powell's tutor) and Reid had earlier produced what appeared to be a black form. H. M. Powell helped to clarify the situation. Among the techniques used were optical crystallography and goniometry but not X-ray diffraction. Nevertheless, it became clear that the 'black form' arose by contamination (usually of the yellow form) by metallic lead.

Mr. Powell had been appointed as a demonstrator in the Department of Mineralogy and Crystallography at Oxford in 1929. There he helped Professor H. L. Bowman to set up a continuously evacuated X-ray tube, the difficulties of which he has described [1] in graphic terms. His first paper reporting X-ray structural results [4] was with his first research student, Dorothy Crowfoot (later Hodgkin), on the organo-metallic halide salts R_2TlX (R = alkyl, X = halide). Apart from special cases, organic structure determination was only just becoming possible at that time. (K. Lonsdale's papers on hexamethyl benzene – one of the first organic structure determinations – had only been published a few years earlier [5–7]). Powell and Crowfoot deduced their structural conclusions mainly from lattice geometry. The spacing between the TlX layers depended on the length of the alkyl chain, R. This and the sideways spacings showed that the chains must be roughly perpendicular to the layers, with

★ Dedicated to Professor H. M. Powell.

insufficient space for free rotation. A more detailed report of the structure of $(CH_3)_2TlI$ appeared later [8], in which it was shown that the two methyl groups were linearly linked to thallium. This was contrasted [9], in 1937, with bent Br—Pb—Br units in the structures of ammonium, rubidium and potassium pentabromoplumbites. Their structures were determined in order to evaluate the valency angle in bivalent lead, in days when characteristic bond lengths and angles were being established.

There was an additional interest for Powell in these isomorphous structures – the structural implications of their stoichiometry. Besides establishing typical lengths and angles for covalent bonds, structural chemists were keen to discover the ranges of coordination numbers that were possible for atoms. This was partly a development from the correlation between coordination numbers and radius ratios for simple ionic structures, and partly a need to establish typical and maximum coordination numbers in metal complexes. H. M. Powell's particular interest in this field was in compounds of unusual stoichiometries. Simple ionic structures usually have even-numbered coordinations derived from highly symmetrical geometrical figures such as tetrahedra and octahedra. For finite (covalently bonded) groups, even these figures cannot be stacked regularly to fill all space, as Powell has mentioned [1]. Greater difficulty might be expected, therefore, with odd coordination numbers, especially since rotational symmetries 5 and 7 are not found in crystallography. So, in an earlier joint paper with Wells [10] on the crystal structure of Cs_3CoCl_5, it was pointed out that the determination was carried out to investigate the possible five-fold coordination of cobalt. In fact, it was found to be tetrahedrally coordinated in $[CoCl_4]^{2-}$ groups, the fifth Cl^- being a separate ion. The atomic positions were determined by the trial-structure method, comparing calculated X-ray intensities with qualitatively observed intensities.

Another paper in the same year by the same authors [11] reported the structure determination of $Cs_3Tl_2Cl_9$, another potentially unusual coordination example, which turned out to have complex $[Tl_2Cl_9]^{3-}$ ions in the form of two $TlCl_6$ octahedra sharing a face. A significant feature in the discussion of this structure was that the corresponding simple salts of tervalent metals of formulae $A_3M^{III}Cl_6$, which contain single $[M^{III}Cl_6]^{3-}$ octahedra, become unstable on increasing the size of M^{III}, because the voids between the octahedra become too large for the cations A^+ that occupy them. This is but one example of the way in which Powell's developing scientific interests intermingled. Not only did this structure relate his interest in voids to that in unusual stoichiometries but it may also have been prompted partly by his earlier studies of thallium compounds. Similarly, the structure determination of Cs_3CoCl_5 not only had links with the later studies of the pentabromoplumbites, mentioned above, but was followed-up by a joint study with A. F. Wells of PCl_5 [12,13]. In that case, the apparent five-fold coordination (actually exhibited in the vapour) is replaced by equal numbers of four-fold and six-fold units in the form of tetrahedral PCl_4^+ and octahedral PCl_6^- ions. A parallel study [14] of PBr_5 showed, however, that here five-fold coordination is avoided in the same way as in Cs_3CoCl_5 by having a tetrahedral PBr_4^+ ion and a separate Br^-. The study of these phosphorus halides foreshadowed a lasting interest in phosphine and phosphole derivatives and arsenic analogues that was pursued in a number of later structure determinations.

The study of unusual coordinations was continued with the structure determination [15] of $Fe_2(CO)_9$ which was found to have a geometry related to that of the $[Tl_2Cl_9]^{3-}$ ion, mentioned above. When the thallium compound had been described [11], it was in terms of octahedra sharing a face, leaving as an open question the degree of covalency in the bonding between Tl and Cl. In the iron enneacarbonyl, covalent bonding was expected and the point at issue was the way in which the nine CO groups were arranged relative to the iron atoms.

It was found that three formed ketonic bridges between two iron atoms and then there were three terminal CO groups on each Fe – a structure different from that previously proposed on chemical grounds. For the first time, what had previously been assumed was experimentally established, that the CO groups bonded through their carbon atoms. The paper reporting this structure was the first of H. M. Powell's to mention techniques which then became almost standard for all structural crystallographers for many years – Weissenberg photographs, eye estimation of intensities by comparison with an intensity scale produced by timed exposures, Patterson and Fourier syntheses using Beevers–Lipson strips (a summation aid devised about three years earlier).

The cage-like nature of that carbonyl structure guided H. M. Powell's thoughts towards his later interpretation of the clathrate structures. Another influence was the structure of $[Fe(CNCH_3)_6]Cl_2 \cdot 3H_2O$ that was one of the next to be determined [16]. This work was carried out as a continuation of the interest in cyanide structures and also to determine the Fe—C bond order (approximately 1.5) now that it was known that CO groups could link by either one or two bonds to iron. It was an unexpected feature of disorder between 2Cl and $3H_2O$, however, that gave a strong lead in the quest for the meaning of the enigmatic dot. The two-fold positions where two Cl^- ions were expected were each occupied by a water molecule. The third H_2O and two Cl^- ions were randomly distributed among the three-fold positions, giving ($2/3Cl^- + 1/3H_2O$) in each. The difficulty of removal of water from this structure is due to its being trapped in the voids inevitably formed by closest packing of octahedral ferrocyanide groups with almost linear arms. The random substitution of Cl^- for H_2O and the lack of any evidence of bonding (e.g. hydrogen bonding) of H_2O, suggested that the water molecules were strongly held in the crystals merely because they were too large to pass between the $CN(CH_3)$ arms surrounding the voids. These ideas, though doubtless in Powell's mind at the time, were only fully expressed later [17] when comparing this structure with the quinol clathrates and related complexes.

Before the publication of this ferrocyanide-type structure, Powell had summarised current knowledge about the stereochemistry of inorganic compounds, together with N. V. Sidgwick, in the Bakerian lecture [18]. In this lecture, rules were also given for predicting stereochemistry according to the total number of valence electrons and the number of covalent bonds formed by the central atom. This simple idea did not receive the recognition it deserved until it was developed into the VSEPR theory by Gillespie and Nyholm. (In passing, it should be noted that the breadth of H. M. Powell's structural interests is well demonstrated by his earlier association with W. Hume-Rothery in classifying and proposing predictive rules for the formation of superlattice structures in alloys [19].)

About the time of this involvement in classifying and predicting alloy superlattices and inorganic stereochemistry, Powell's investigation of the meaning of the dot in molecular complex formulae took a new turn, at the suggestion of D. Ll. Hammick. He began a series of investigations of what were then known as 'molecular compounds' of polynitro-compounds with aromatic hydrocarbons and related substances. Picric acid had long been used in the identification of aromatic hydrocarbons from the melting points of the complexes it formed with them. Picryl halides form similar complexes and have the advantage, for crystal structure determination, of introducing a heavy atom. Unfortunately, these complexes show disorder [20] and do not permit the determination of atomic coordinates. Nevertheless, it was possible to discount (from the approximately van der Waals spacings between layers of the components and from melting points and diffuse X-ray reflections) the suggestion that had been made by Weiss [21], that ionic complex molecules are formed by transfer of an electron from the aromatic donor to the polynitro-compound. (How near Weiss was to Mulliken's later

accepted charge-transfer formulation of these complexes!) The publication of this work must have been held up for some time because of its inability to reveal detail, since it is hinted at in a paper published three years earlier [22] on picryl iodide itself. The approximate results that could be published were a necessary response to the appearance of Weiss's paper. Meanwhile, the non-disordered crystal structure of the related complex between *p*-iodoaniline and 1,3,5-trinitrobenzene had been published [23] 'out of [the] natural order' because of its significance and completeness. That structure determination must have been one of the first in which Fourier sections and lines were calculated from three-dimensional X-ray intensities. It also represented the first detailed study of a charge-transfer complex and it established the existence of stacks of alternate, parallel, donor and acceptor molecules with approximately van der Waals separations, now accepted as characteristic of such complexes. To quote again from the paper: 'All structural formulae proposed for these ['molecular'] compounds which involve a [covalent] bond are therefore excluded at once,...'. It seems strange now, that there was still such confusion between inter- and intra-molecular bonding that it was necessary then to be so dogmatic.

It must have been about this time that the happy accident occurred, already described by Powell [1], that resulted in the crystallisation of the complex $3C_6H_4(OH)_2 \cdot SO_2$ and reminded him of the existence of a series of quinol complexes of unusual stoichiometry. A second happy accident, also mentioned by Powell [1] and enlarged upon in this issue [24], provided the opportunity of carrying out the 'academic exercise' of exploring the meaning of the dot in the formulae of this series of complexes. Little did the authors know that they were opening-up the whole new science of the study of clathrate compounds, to which this *Journal* is largely devoted. This area of Powell's work, which has won for him the widest acclaim, is well documented in this *Journal* and need not be pursued in this article. Two further aspects only will be mentioned. The first is the evident pleasure it gave to Professor Powell that it led, amongst other things, to the ability to bring about the resolution of racemic mixtures of optical enantiomers [25,1]. The second is the further happy accident, once pointed out to the author by Professor Powell, that the discovery of the clathrates should fall to a scientist who, through his interest in languages, should know exactly the right name to give them.

It will be realised that many aspects of H. M. Powell's work, especially the more recent and therefore better known and more accurate structure determinations, have not been mentioned here. This does not imply that they are any less important or less wide-ranging but simply that they are more accessible and that most of them arise from the early interests described here. The purpose of the present article has been to draw attention to the less generally recognised involvement of Professor Powell in shaping early fundamental knowledge of the nature of bonding and of the geometrical significance of stoichiometric formulae, with or without the enigmatic dot.

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