

Four lessons from my very early days in crystallography: The lasting impact of a few selected 'first structures' on my path in science

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As a new, uninitiated member of Al Cotton's group in the Summer of 1964, I was assigned the task of learning how to do crystal structures, starting with the synthesis and growth of crystals of rhenium triiodide. The synthesis was troublesome but eventually I got some small needles of ReI₃, and collected Weissenberg film packs in order to measure the intensities. I found the space group to be P2₁ or P2₁/m. I processed the data after punching the intensities onto cards, and used the reliable Patterson Function to solve the structure...all seemed to go well. But I had a sensible-looking structure that would not refine below a conventional R of 25-30%. I could not budge it! A highly creative and intelligent visitor to the lab, Leo Becka, looked at the solution, pronounced it likely correct, and suggested that there was a problem with the program...read the FORTRAN, Bruce! Wow. It was about 2000 statements...but not hard to learn how it worked. I found an error that prevented the structure from refining...great! Lesson 1 was that one had to learn to be a program guy in those days. The structure of ReI₃ was NOT publishable (decent R for the time, ca. 8-9%, but low resolution). So, off to grow more, and good xtals. That took 2.5 years(!), but R was 4.4%.¹ Lesson 2: Thus I found that there was a crystal growth method that was always "guaranteed" to work.² The other events, all described in detail, are Lesson 3: use programming skills to reduce the number of parameters using rigid phenyl groups (my fifth structure),³ and carry that on to studies of hindered rotation in crystals.⁴ Lesson 4 describes the results following structure determinations of X-ray sensitive cobalt complexes (my sixth structure⁵) using CuK α radiation and a lucky conversation with a famous organic chemist Arthur Birch, the ANU School of Chemistry Dean: that encounter set me on a career of 50+ years of studying reactions in crystals. 1. Bennett, M. J.; Cotton, F. A.; Foxman, B. M. *Inorg. Chem.* 1968, 7, 1563-1569. 2. Cotton, F. A. *My Life in Chemistry : More Fun Than Fun*; Falvello, L. R.; Foxman, B. M. Murillo, C. A.; Murillo, D. Assoc. Eds.; Elsevier, Waltham, MA, 2014, p.94. 3. Cotton, F. A.; Eiss, R.; Foxman, B. M. *Inorg. Chem.* 1969, 8, 950-957. 4. Bennett, M. J.; Hutcheon, W. L.; Foxman, B. M. *Acta Crystallogr. Sect. A* 1975, A31, 488-494. 5. Buckingham, D. A.; Foxman, B. M.; Sargeson, A. M.; Zanella, A. J. *Am. Chem. Soc.* 1972, 94, 1007-1009; Buckingham, D. A.; Clark, C. R.; Foxman, B. M.; Gainsford, G. J.; Sargeson, A. M.; Wein, M.; Zanella, A. *Inorg. Chem.* 1982, 21, 1986-1997.