

Adventures and Surprises in X-ray Diffraction Experiments and Crystal Structure Analyses. – Selected Examples.

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It is said that a crystal structure analysis of small molecules can nowadays be done within some three to six hours, when using a modern area detector diffractometer system and fast computers with suitable software packages. The fast increasing number of deposited crystal structures at the CCDC (Cambridge, now more than 250000 structures) supports this assumption. On the other hand it seems that important crystallographic knowledge is slowly declining and being forgotten as more and more service people are using and trusting the “black box” software. The detection of an increasing number of published regular structures that were assigned with wrong space groups (see e.g. R.E. Marsh) should be noticed in this sense. These are helpful publications, also H. Flack’s and G. Bernardinelli’s comments on evaluating the absolute-structure and absolute-configuration, as well as A. Spek’s PLATON program that allows for powerful space group and data validation checks. These informations should reduce the number of structural papers with this kind of errors.

However, sometimes a structure determination is not a routine job. Some adventurous and surprising results of crystal structure analyses are presented, which in no way could be performed in a couple of hours: 1. three naturally occurring contact allergens with no or incomplete chemical information showing twinning, polytype diffraction and superstructure effects, 2. a blue and a green form of compositionally disordered Ti-complexes, 3. a Keggin-type structure with four non-coordinating hypoxanthine and ten water molecules were found instead of an expected Mo-hypoxanthine-complex, 4. Na^+ instead of water was detected in a Zn-acyclovir complex, 5. a remeasurement of $\text{Cu}(\text{OH})_2$ established the structure to be non-centrosymmetric, 6. an expected 3D network structure turned out to consist of five independent complexes and 28 water molecules, 7. two strongly disordered W-complexes are presented, where the higher symmetry had to be applied, 8. a rare case of 11 independent Re-complexes in space group $P21/a$ with $Z=44$ was completed including some disorder, 9. two merohedrally twinned structures are finally presented, one of which is a Fe-mercaptopurine complex, the other is a dimeric Mn-phosphinoethane complex with a tetragonal lattice but with true monoclinic symmetry and angle beta being near 90° .

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