PS02.01.13 TROUBLESOME PERCHLORATES. Rita Gronbaek Hazell and Alan Hazell, Dept of Chemistry, University of Aarhus, DK3000 Aarhus C, Denmark.

Complexes of transition metals are often crystalized as the perchlorate salts, as these usually gives good crystals. Crystallographers are rarely impressed as experience tells us that these anions are often disordered to some degree. Over the years we have developed and adapted the following routines to facilitate work on disordered groups;

1. Fourier synthesis calculated on a sphere of desired radius around an atom, to get some idea as to how (dis)ordered the group is.
2. A freely rotating group can be treated by giving the chlorine atom a scattering factor calculated as: \( f_{\text{rot}}(s) = f_C(s) + 4f_O(s)\sin(4\pi s)/4\pi s \)
3. Disorder between 2 or more distinct orientations is dealt with by constraint refinement according to Pawley (1971) using the symmetric/identical molecule constraints and restricting the occupancies to add up to 1.0.
4. Thermal motion is dealt with in the TLS or more usually TLX model to save parameters.
5. Large thermal motion together with geometric constraints requires that the TLS model is expanded to include third cumulants (Zachariasen, 1945).

For special needs the user will however still have to read the manual with a minimum of effort. Some of the procedures described here may be adapted into the constraint refinement more user-friendly.

The refined thermal displacement parameters \( u(K), u(Ta), u_{11}(O) \) and \( u_{22}(O) \) were found systematically dependent on both wavelength and absorption coefficient. While the relative distribution of the \( u \)-values along the bonds remained unchanged, the individual values showed an approximately linear positive correlation with the absorption coefficient varying between \( \mu = 0.029 \) and \( \mu = 0.237 \) Å. At present, there is no obvious explanation for this behaviour. Results of a detailed analysis being under progress will be presented.

PS02.01.15 MERIEDRIC TWINNING IN NEW CoSi3P3 SEMICONDUCTING COMPOUND. CRYSTAL STRUCTURE AND RAMAN SPECTROSCOPY. H. Vincent, J. Kreisel, O. Chauix-Pluchery and R. Madar LMGP (URA CNRS 1109), ENS de Physique de Grenoble, 38402 St Martin d’Hères, France.

New cobalt phospho-silicide CoSi3P3 has been synthesized and its crystal structure determined by single crystal X-ray diffraction. CoSi3P3 crystallizes with the apparent orthorhombic symmetry: \( a = 5.900(1) \) Å, \( b = 5.703(1) \) Å, \( c = 12.736(1) \) Å. Only one extinction rule is observed, it concerns reflections \( 0k0 \) with \( k = 2n+1 \). Wilson statistic and non-linear optical tests excluding some symmetry center, attempt to solve the structure in \( P2_12_12_1 \) group was done but unsuccessful. Assuming the presence of pseudo \( 2 \)

emergence of the weak \( 2 \)

reflection analysis

The routine are quite general and care is taken to ensure that standard deviations of derived as well as refined parameters are calculated. The computer programs used at Aarhus stem from SUNY Buffalo and include modified ORFLS, ORFFE and FORDAP. Locally we have a menu driven system to run standard calculations with a minimum of effort. Work is still going on trying to make in particular the constraint refinement more user-friendly.

The crystal structure can be described by zigzag chains of octahedra occupied by Co atoms and zigzag chains of tetrahedra occupied by P or Si atoms. All these infinite chains are parallel to the b-axis. Two chains of a same kind are separated each other by a chain of other kind. Magnetic susceptibility and electronic conductivity have been measured between 300 K and 10 K. CoSi3P3 is diamagnetic at room temperature and paramagnetic below 60 K. CoSi3P3 is semiconducting at room temperature with an energy gap of about 0.12 eV.

PS02.01.16 TRANS-5-HYDROXYCYCLOOCTYLTRIMETHYLSTANNANE: A STRUCTURE IN SPACEGROUP Cc DESCRIBED AS A DISPLACIVE MODULATION OF A P2_1/c PARENT STRUCTURE. A. C. Willis and A. D. Rae. Research School of Chemistry, Australian National University, Canberra, ACT, Australia, 0200

\( (\text{CH}_3)\text{SnC}_2\text{H}_4\text{OH} \) crystallises in spacegroup Cc with 16 molecules per unit cell. a = 13.786(4) \( b = 13.856(3) \) \( c = 28.917(2) \) \( \beta = 100.47(1)^\circ \). An initial solution in spacegroup \( P2_1/c \), \( Z = 4 \), used only the strong \( h \) even, \( k \) even reflections. This superimposes molecules separated by \( a/2 \) in the true structure. The Sn and C atoms appeared as full weight atoms. The O and 4 remaining C atoms each appeared as a 1:1 disorder between sites separated by over 1 Å. This was interpreted as two identical molecules related by a 120° rotation about the \( \text{Co} = \text{Si} = \text{C} \) bond. Ordering the disorder to create a model for the weak \( h \) odd, \( k \) odd reflections allows 4 possible structures. This is predicted from the doubly degenerate irreducible representation associated with the modulation vector \( a^*b^* \). Local inversion centres are maintained.