structures of organic and coordination compounds

9.8.35 structure of a twinned crystal of wolffram's red salt

Wolffram's red salt [Pt(C2H4N4)Cl2]·2Cl is a typical example of halogen-bridged one-dimensional mixed-valence complexes. The crystal is characterized by linear chains of alternate stacks of octahedral and square planar ions. His-stacks, however, occur within the chains: the structure can be thought to consist of averaged octahedral ions with half-weighted Cl atoms and to have a half-period chain axis. This subcell structure was reported as pseudo-tetragonal, the space group 4mm (Craven & Hall, Acta Cryst., 1961, 14, 475-480). We report a twinning of the crystal. The pseudo-tetragonal reflections with x,y,z split as illustrated in Fig. 1: the twinned crystal consists of four individuals, c being the twin axis of 1/2 rotations. The structure was redetermined with intensity data of a twin component: monoclinic, the space group Im, z=1; a = 13.302(3), b = 13.337(5), c = 5.391(1) Å, β = 90.98(3)°. Fig. 2 shows a projection of the structure along c; Wolffram's red is iso-morphous with the bromo analogue Reihlen's green (Brown & Hall, Acta Cryst., 1976, B32, 279-281).

9.8.36 Neutron-diffraction study and refinement of structure based on combined x-ray and neutron data of Dichloro(tetrapyridine)platinum(II) trihydrate, [Pt(C2H4N4)Cl]2·2Cl·3H2O. By C. H. Wei, Biology Division, and W. M. Busing, Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA.

The title compound crystallizes with four formula units in a cell of symmetry C2 with a = 12.711(1), b = 12.856(1), c = 16.600(2) Å and β = 118.586(8)°. Its structure by X-ray diffraction has been reported (C. H. Wei and B. S. Hingerty, Acta Cryst. (1984) A40, C-309). Although the final R(F) value was 0.021, the water H atoms were not found. Recrystallization of the compound from pyridine-water solution produced suitable crystals for a neutron-diffraction study. The neutron-diffraction data were collected at ORNL to 0.86 Å with neutron wavelength of 1.537 Å. Six water H atoms were first located from a difference map. Parameters of 56 atoms with anisotropic thermal motion were refined based on a combination of 7429 X-ray data with isotropic extinction and 1335 neutron data with anisotropic extinction. The 515 variables were adjusted by program ORFLS with user subroutine WEIGHT selecting X-ray or neutron scattering factors for the different data sets. A final R(F) of 0.022 was obtained for the combined data. All water H atoms make hydrogen bonds with neighboring Cl- ions and each Cl- is linked to three atoms of different water molecules, thus forming a three-dimensional network. The H...Cl distances and H...-Cl angles range from 2.16(1) to 2.38(1) Å and 105.5(4) to 131.9(4)°, respectively. The average C-H and O-H distances are 1.078(2) and 0.943(5) Å, and the four H atoms of pyridine rings that form a square-planar array around the metal are in a plane to within 0.026(1) Å. (*Research supported by the Office of Health and Environmental Research and the Division of Materials Sciences, Office of Basic Energy Sciences, US Department of Energy, under contract DE-AC05-84OR21400 with the Martin Marietta Energy Systems, Inc.)