

09.4-35 STRUCTURE OF A TWINNED CRYSTAL OF WOLFFRAM'S RED SALT. By S. Sato and K. Kobayashi, The Institute for Solid State Physics, The University of Tokyo, Japan.

Wolffram's red salt  $[\text{Pt}(\text{C}_2\text{H}_5\text{NH}_2)_4\text{Cl}_2][\text{Pt}(\text{C}_2\text{H}_5\text{NH}_2)_4\text{Cl}_4 \cdot 4\text{H}_2\text{O}]$  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. Mis-

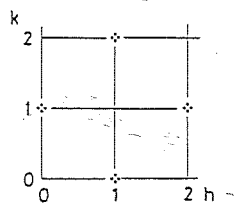


Fig. 1. hkl.

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  $I4mm$  (Craven & Hall, *Acta Cryst.*, 1961, **14**, 475-480). We report a twinning of the crystal. The pseudo-tetragonal reflections with  $l \neq 0$  split as illustrated in Fig. 1: the twinned crystal consists of four individuals,  $c$  being the twin axis of  $\pi/2$  rotations. The structure was redetermined with intensity data of a twin component: monoclinic, the space group  $Im$ ,  $Z=1$ ;  $a=13.302(3)$ ,  $b=13.337(5)$ ,  $c=5.391(1)\text{\AA}$ ,  $\beta=90.98(3)^\circ$ . Fig. 2 shows a projection of the structure along  $c$ ; Wolffram's red is isomorphous with the bromo analogue Reihlen's green (Brown & Hall, *Acta Cryst.*, 1976, **B32**, 279-281).

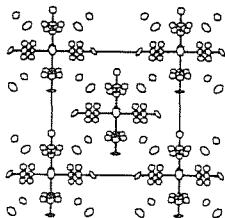


Fig. 2.

09.4-36 NEUTRON-DIFFRACTION STUDY AND REFINEMENT OF STRUCTURE BASED ON COMBINED X-RAY AND NEUTRON DATA OF DICHLORO(TETRAPYRIDINE)PLATINUM(II) TRIHYDRATE,  $[\text{Pt}(\text{C}_5\text{H}_5\text{N})_4]^{2+} \cdot 2\text{Cl}^- \cdot 3\text{H}_2\text{O}$ .\* BY C. H. Wei, Biology Division, and W. R. 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  $Cc$  with  $a = 12.711(1)$ ,  $b = 12.856(1)$ ,  $c = 16.600(2)\text{\AA}$  and  $\beta = 118.544(8)^\circ$ . Its structure by X-ray diffraction has been reported (C. H. Wei and B. E. 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  $\text{\AA}$  with neutron wavelength of 1.537  $\text{\AA}$ . 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 3429 X-ray data with isotropic extinction and 1336 neutron data with anisotropic extinction. The 515 variables were adjusted by program ORXFLS4 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  $\text{Cl}^-$  ions and each  $\text{Cl}^-$  is linked to three atoms of different water molecules, thus forming a three-dimensional network. The  $\text{H} \cdots \text{Cl}^-$  distances and  $\text{H} \cdots \text{Cl}^- \cdots \text{H}$  angles range from 2.16(1) to 2.38(1)  $\text{\AA}$  and 65.5(4) to 134.9(4)°, respectively. The average C-H and O-H distances are 1.078(2) and 0.943(5)  $\text{\AA}$ , and the four N atoms of pyridine rings that form a square-planar array around the metal are in a plane to within 0.026(1)  $\text{\AA}$ . (\*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.)

09.4-37 CHARACTERIZATION OF SUPPORTED OLEFIN POLYMERIZATION CATALYSTS BY X-RAY DIFFRACTION. By H. Österholm, P. Sormunen and B. Löfgren, Neste Oy, Technology Centre, SF-06850 Kulloo, Finland

A modern Ziegler-Natta catalyst system for the polymerization of highly isotactic alpha olefins consists of a magnesium halide carrier, a titanium halide, an electron donor (Lewis base) and of a co-catalyst. The catalytic system is studied at different stages with a wide angle X-ray diffractometer, equipped with a special sample holder for air-sensitive compounds. The catalyst carrier has been prepared by mechanical activation from magnesium dichloride and by chemical activation from a magnesium dialkyl. The electron donors studied are a monoester, ethyl benzoate, and a diester, di-isobutyl phthalate. The formation of a magnesium dichloride carrier with a highly amorphous structure is a prerequisite for obtaining an active catalyst. In chemically activated carriers the stacking of the  $\text{Cl-Mg-Cl}$  layers along the  $c$ -axis is limited to the dimensions of a unit cell while mechanically activated magnesium dichloride results in larger crystallite size. The donor forms a complex with the surface atoms of the carrier, this new phase can be observed by X-ray diffraction only when very high amounts of donor have been used. The titanium tetrachloride treatment increases the degree of order in the carrier. This can be observed from the differences in the halo at a  $d$ -spacing between 3.0 and 2.5 Angstroms in the X-ray diffractogram.