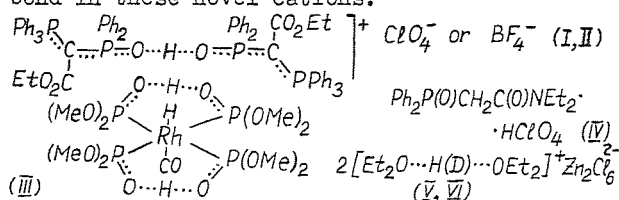


04.6-4 X-RAY INVESTIGATION OF CRYSTALS WITH STRONG HYDROGEN BONDS. By M.Yu. Antipin and Yu.T. Struchkov, Nesmeyanov Institute of Organoelement Compounds of the USSR Academy of Sciences Moscow USSR

Data of low temperature ( $-120^{\circ}\text{C}$ ) X-ray studies have been used to analyze the specific features of geometry and thermal vibrations in a large series of crystal structures with very strong and probably symmetrical H-bonds of the O...H...O type (O...O 2.4-2.5 Å). This series includes complexes of phosphoryl compounds with acids, phosphite complexes, tautomeric organophosphorus compounds, etherates etc., whose typical examples are represented by compounds I-VI. Thermal ellipsoids of the central H-atom in the hydrogen bonds of these structures correspond to intense vibrations of this atom preferably along the O...O direction. Precise X-ray data can give a qualitative description of such movement. On the contrary, in the case of weak or medium strength H-bonds thermal vibration of H-atom occur preferably in the direction normal to the O...O line. Isotopic substitution in V and VI (exchange of H for D) does not cause an increase of the O...O distance which is in both cases equal to 2.396 Å and this result is a good evidence for a single-minimum potential of the H-bond in these novel cations.



The molecule possesses a symmetry center. The palladium atom, occupying the center of symmetry, is coordinated in a square-planar fashion to the Cl atoms and the N atom of pyridine ring.

There is an intramolecular hydrogen bond  $\text{N}_2\text{-H}_{21}\dots\text{Cl}_1 = 3.448(6)\text{Å}$  and on the other hand the molecules are packed in the crystal in a network of hydrogen bonds, there being between the latter bifurcated ones as indicated in the following table:

DONOR-H		DONOR...ACCEPTOR	
N2	-H21	N2	....Cl1 (0)
0.757(.085)		3.448(.006)	
N2	-H21	N2	....Cl1 (1)
0.757(.085)		3.378(.006)	
N2	-H22	N2	....Cl1 (2)
0.910(.098)		3.429(.006)	
H...ACCEPTOR		DONOR-H.....ACCEPTOR	
H21	...Cl1 (0)	N2	-H21 ...Cl1 (0)
2.998(.094)		120.82( 7.70)	
H21	...Cl1 (1)	N2	-H21 ...Cl1 (1)
2.776(.088)		138.20( 8.43)	
H22	...Cl1 (2)	N2	-H22 ...Cl1 (2)
2.550(.094)		162.44( 7.58)	

EQUIVALENT POSITIONS:

- (0) X,Y,Z,  
 (1) -X,-1, -Y,-Z  
 (2) +X,+Y,+Z+1

04.6-5 X-RAY CRYSTAL AND MOLECULAR STRUCTURE OF

TRANS-BIS(2-AMINOPYRIDINE) DICHLOROPALLADIUM(II)

M.C. Navarro-Ranninger\*, S. Martínez-Carrera and S. García-Blanco.

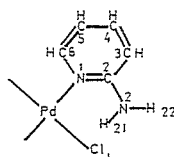
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The title compound have been prepared according to (1) Suitable crystals were obtained by recrystallization from dimethylformamide.

Crystal data:  $\text{Pd}(\text{C}_5\text{N}_2\text{H}_6)_2\text{Cl}_2$ ,  $M = 235.97$ ,  $a = 5.922(2)$ ,  $b = 16.589(12)$ ,  $c = 6.722(3)\text{Å}$ .  $\beta = 104.52(3)^\circ$ .  $V = 639.3(6)\text{Å}^3$ ,  $D_x = 1.226\text{ Mg m}^{-3}$ ,  $F_2/n$ ,  $Z = 2$ .

Intensities were measured on a CAD-4 diffractometer with  $\text{MoK}\alpha$  radiation. The structure was solved by Patterson and Fourier methods and refined anisotropically by full matrix least-squares technique to  $R = 0.050$ ,  $R_w = 0.060$  for 1737 reflections ( $I \geq 2\sigma(I_0)$ ). The hydrogen atoms were found from the difference Fourier syntheses. The final  $R = 0.045$ ,  $R_w = 0.054$ , ( $w = 1.0$ ).



(1) C. Gómez, A. Alvarez, C. Navarro-Ranninger, J.R. Masaguer, Trans. Met. Chem. (in press).

04.6-6 STRUCTURE AND HYDROGEN ORDERING IN ICES VI, VII, AND VIII BY NEUTRON POWDER DIFFRACTION. By

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The ice phase diagram is extremely rich, due partly to the structural versatility inherent in the tetrahedral hydrogen-bonding possibilities of the water molecule and partly to the possibilities of proton ordering. Especially the high pressure phases have been used to explore details of the water-water interaction. Recently, the cell volumes,  $c/a$  ratios, and proton orderings have been used to test model water-water potential functions that are extensively used in computer simulations of the pure liquid and more complex aqueous solutions. Many uncertainties remain, however, concerning the details of the structures of several of these phases. This is especially so for the highest pressure phases, where implications concerning proton ordering from dielectric and thermodynamic measurements are sometimes in conflict with the limited crystallographic data available. Moreover, much of this crystallographic data was collected on samples quenched under pressure to liquid nitrogen temperatures, and then recovered to ambient pressure, rather than on samples within the stability ranges of the respective phases. Although it appears to be generally assumed that such recovered samples are structurally similar to the original stable phases, the possibility remains that structural changes (especially of the hydrogen ordering) may occur on recovery, and these might be responsible for some of the apparent discrepancies between crystallographic and other results. These uncertainties can in principle be resolved by neutron crystallography. The recent development of high pressure cells for neutron work allows powder measurements to be taken throughout the whole of the ice phase diagram up

to pressures of about 3 GPa, and down to liquid helium temperatures. We present here the results of high pressure powder measurements on the three D<sub>2</sub>O ice phases that have interpenetrating sublattices (ices VI, VII and VIII). The mode of ordering of tetragonal ice VIII (SG: I4<sub>1</sub>/amd) is clearly established, and no evidence is found of partial ordering as the temperature is raised. Ice VII is accurately cubic (SG: Pn3m) with D<sub>2</sub>O molecules disordered around their center of mass; there is no evidence of partial ordering at any temperature. The water molecule geometry is normal in both phases, and the hydrogen-bonded first neighbour in ice VIII is confirmed to be more distant than the first non-bonded neighbour. The transition temperature between the two phases occurs at 263 ± 2 K, some 11 K lower than expected. Hydrogen bond lengths in both phases are equal at the transition. Although the ice VI data is less good, we can see no evidence of the antiferroelectric ordering proposed by Kamb from work on recovered samples. Our results are consistent with thermodynamic measurements indicating disorder in ice VI at 193 K. We conclude that the orientational ordering behaviour of these high pressure ices is simpler than thought previously. For our ice VI result to be consistent with those of Kamb, his antiferroelectric ordering must be an artifact of the recovery process, thus throwing doubt on the validity of structural ordering data obtained on samples recovered to ambient pressure.

04.6-7 HYDROGEN-BOND RESEARCH USING THE CAMBRIDGE STRUCTURAL DATABASE. Robin Taylor and Olga Kennard, Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K.

Analysis of data in the Cambridge Structural Database provides detailed information about the basic factors governing hydrogen bond geometry. H...A distances can be correlated with the nature and crystallographic environment of the donor and acceptor groups - for example, R<sub>3</sub>N<sup>+</sup>H...O bonds are found to be shorter than H<sub>3</sub>N<sup>+</sup>-H...O bonds. D-H...A angles have an energetic preference for linearity or near-linearity, particularly when the H...A distance is short. There is a slight preference for hydrogen bonding in the directions of sp<sup>2</sup> lone pairs, but it is arguable whether a similar preference exists for sp<sup>3</sup> lone pairs. Donor and acceptor valence bonds appear to be lengthened by hydrogen-bond formation, but this may be an artefact of librational phenomena. Hydrogen bonds involving C-H donors or the 3-centre ('bifurcated') arrangement are more common than previously supposed.

04.6-8 CRYSTAL STRUCTURE OF M<sup>II</sup>H<sub>10</sub>(AsO<sub>4</sub>)<sub>4</sub> COMPOUNDS AND HYDROGEN BONDING (M<sup>II</sup> = Mg, Mn, Ni, Cu and Zn). By M. Chiadmi and D. Tran Qui, Laboratoire de Cristallographie, C.N.R.S., associé à l'U.S.M.G., 166 X, 38042 - Grenoble Cedex, France.

Acidic orthoarsenate M<sup>II</sup>H<sub>10</sub>(AsO<sub>4</sub>)<sub>4</sub> compounds (M<sup>II</sup> = Mg, Mn, Co, Ni, Cu and Zn) have been prepared and single crystal grown. X-ray data show that all the series members belong to space group P1 and have very close unit cell parameters suggesting normally isomorphism between these salts. Crystal structure of CuH<sub>10</sub>(AsO<sub>4</sub>)<sub>4</sub> (a = 5.391(3), b = 7.631(4), c = 8.298(5), α = 105.84(4), β = 97.62(3) and γ = 93.64(10)) has been established including hydrogen positions and refined to a final R factor 3.9 % for 2158 reflections. The structure consists of CuO<sub>6</sub>-AsO<sub>4</sub> chain parallel to a-axis. CuO<sub>6</sub> octahedra and AsO<sub>4</sub> tetrahedra are linked together by oxygen corners sharing. Hydrogen localizations confirm the existence of biacidic and triacidic groups: AsO<sub>2</sub>(OH)<sub>2</sub> and AsO(OH)<sub>3</sub>.

It was also observed that the triacidic AsO(OH)<sub>3</sub> orientation with respect to CuO<sub>6</sub>-AsO<sub>4</sub> chain is significantly different in CuH<sub>10</sub>(AsO<sub>4</sub>)<sub>4</sub> crystal structure and in that of CdH<sub>10</sub>(AsO<sub>4</sub>)<sub>4</sub> (a = 5.69(5), b = 7.42(4), c = 8.60(6), α = 105.17(1), β = 95.13(5), γ = 91.85(5), (Boudjada et al., Acta Cryst. (1980), B36, 133-135)). This structural distortion will be discussed in terms of hydrogen bonding.

04.6-9 HYDROGEN BONDING IN ACID SALTS OF MESO-TARTARIC ACID. By P.F.W. Stouten, A.J.A.R. Blankensteyn & J. Kroon, Laboratorium voor Kristal- en Structuurchemie, Rijksuniversiteit, Padualaan 8, Utrecht, The Netherlands.

In acid salts of dicarboxylic acids H<sub>2</sub>Y we should expect the anion in MHY to have one carboxyl group ionized, the other not. In this case the carboxyl groups are linked by H bonds, which are essentially non-symmetric; they are called B-type bonds [Speakman, Structure and Bonding (1972) 12, 141]. However, frequently another variant is found in which inter-carboxyl H bonds lie across crystallographic symmetry elements; according to Speakman they are classified as A-type bonds.

Acid salts of meso-tartaric acid display a wide variety of H-bond patterns. We already reported the mixed A/B type of KHC<sub>4</sub>H<sub>4</sub>O<sub>6</sub> [Kroon & Kanters, Acta Cryst. (1972) B28, 714] and the B-type acid salt PhCH(NH<sub>2</sub>).C<sub>4</sub>H<sub>5</sub>O<sub>6</sub> [Blankensteyn, Moerman, Ouwkerk & Kroon, Coll. Abstracts E.C.M. 8 (1983) 161].

We now have solved the crystal structure of the superacid salt of composition NaH<sub>3</sub>(C<sub>4</sub>H<sub>4</sub>O<sub>6</sub>)<sub>2</sub>, which also appears to be of a mixed A/B type and that of LiHC<sub>4</sub>H<sub>4</sub>O<sub>6</sub>.H<sub>2</sub>O with unusual cyclic H-bonded carboxyl dimer formation.

NaH<sub>3</sub>(C<sub>4</sub>H<sub>4</sub>O<sub>6</sub>)<sub>2</sub>, monoclinic, P2<sub>1</sub>/c, a=6.514(1), b=9.193(3), c=9.440(3) Å, β=96.38(2)°, v=561.8 Å<sup>3</sup>, Z=2, λ(CuKα)=1.5418 Å, 992 unique reflections [I ≥ 2.5σ(I)], current R=0.065.

LiHC<sub>4</sub>H<sub>4</sub>O<sub>6</sub>.H<sub>2</sub>O, monoclinic, P2<sub>1</sub>/c, a=4.886(1), b=25.361(3), c=5.310(1) Å, β=84.19(1)°, v=654.6 Å<sup>3</sup>, Z=4, λ(CuKα)=1.5418 Å, 1218 unique reflections [I ≥ 2.5σ(I)], current R=0.078.