– deux déduits par les transformations x $\frac{1}{2}-y$ $\frac{1}{2}+z$ et
x, $\frac{1}{2}-y$ $z-\frac{1}{2}$, à 7,1 Å.

Nous remercions vivement Madame Lajzérowicz qui
a constamment suivi et conseillé ce travail et Monsieur
Michel Thomas, Ingénieur à l'Institut Laue Langevin de
Grenoble qui a participé aux mesures sur le diffractomètre
quatre cercles Siemens.

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The crystal structure of tetraphenylarsonium diaquohydrogen dichloride.

By B. D. FAITHFUL and S. C. WALLWORK, Department of Chemistry, The University of Nottingham, England

Crystals of $(C_6H_5)_4As^+(H_2O\ H\ OH_2)^+2Cl^-$ contain 4 formula units in each cell of dimensions $a=13\cdot08$, $b=16\cdot96$, $c=16\cdot98$ Å, $\beta=140°26'$ with space group $P2_1/c$. Two independent diaquohydrogen ions lie across centres of symmetry, the water molecules being linked by strong central hydrogen bonds of length about 2·4 Å. The peripheral hydrogen atoms of each diaquohydrogen ion form hydrogen bonds of length about 2·95 Å to two pairs of chloride ions in trans positions relative to the O–O axes.

As part of a series of studies on strongly hydrogen-bonded
inorganic ions a crystallographic examination was carried
out on what was originally thought to be tetraphenyl-
arsonium hydrogen dichloride. However, when the calcu-
lated and observed densities of the crystals were compared
it was found that the substance must be a dihydrate. It
was nevertheless decided to continue the crystal structure
determination to see whether there were HCl_2^- ions in the
hydrated material or whether the proton was associated
with the water molecules.

Suitable crystals were obtained by slowly cooling a satur-
ated solution of tetraphenylarsonium dichloride in $10M$
hydrochloric acid. In all, 1999 significant intensities were
measured on a linear diffractometer using a needle-shaped
crystal about 0·3 mm diameter sealed in a thin-walled glass
capillary. The intensities were corrected by Lorentz and
polarization factors but not for absorption or extinction.

Crystal data

$(C_6H_5)_4As^+H_5O_2^+2Cl^-$. M.W. 491·3
Monoclinic.
$a=13\cdot09$, $b=16\cdot96$, $c=16\cdot98$ Å, all $\pm0\cdot01$ Å,
$\beta=140\cdot4\pm0\cdot2°$;
$U=2402$ Å^3, $D_m=1\cdot35$ g.cm^{-3}, $Z=4$, $D_c=1\cdot358$ g.cm^{-3};
$F(000)=1008$. Mo $K\alpha$ $(\lambda=0\cdot7107$ Å), $\mu=17\cdot3$ cm^{-1}.
Absent spectra $h0l$ when l odd, $0k0$ when k odd. Space
group $P2_1/c$ (No. 14).

The positions of the arsenic atoms were found from a
three-dimensional Patterson synthesis and a Fourier elec-
tron-density map phased on the arsenic atoms revealed the
positions of the chloride ions. The positions of the carbon
and oxygen atoms were found in a succession of least-

squares refinements and Fourier calculations. When all the
non-hydrogen atoms had been located further least-squares
refinement was continued, first with individual isotropic
thermal parameters and then, in the last few cycles, with
anisotropic thermal parameters for the arsenic atoms and
the chloride ions. The refinement converged with $R=0\cdot082$
for 132 positional, thermal and scale parameters and 1999
intensities. The final calculated structure factore are com-
pared with the observed values in a Table which has been
deposited.*

The atomic positions are given in Table 1 and hydrogen
bond lengths and angles are shown in Fig. 1. Fig. 2 is a
general view of the structure.

The structure consists of zigzag strings of tetraphenyl-
arsonium ions with their mean lines parallel to [101] and
passing through 000 and $0\frac{1}{2}\frac{1}{2}$, interspersed with ribbons of
hydrogen-bonded oxygen atoms and chloride ions with
their mean lines also parallel to [101] but passing through
$0\frac{1}{2}0$ and $00\frac{1}{2}$. Each hydrogen-bonded ribbon has the struc-
ture shown in Fig. 1 consisting of fused pairs of non-planar
pentagons sharing a strongly hydrogen bonded O–H–O
side with (at least statistically) a central proton. These fused
pairs of pentagons are then linked point-to-point by further
strong O–H–O hydrogen bonds, with again a central proton,
to give the infinite ribbons. No attempt has been made to
locate the hydrogen atoms in the structure but, assuming
that those in the hydrogen bonds lie approximately in the

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* This table has been deposited with the National Lending
Library, England, as Supplementary Publication No. 30008.
Copies may be obtained through the Executive Secretary,
International Union of Crystallography, 13 White Friars,
Chester CH1 1NZ, England.

Table 1. *Atomic coordinates and (in parentheses) their standard deviations*

	x/a	y/b	z/c
As	0·3221 (2)	0·0838 (1)	0·2592 (1)
Cl(1)	0·6647 (6)	0·1230 (2)	0·2440 (4)
Cl(2)	0·7860 (5)	−0·1302 (3)	0·2330 (5)
O(1)	0·4336 (25)	0·0444 (12)	0·0027 (17)
O(2)	0·8601 (14)	−0·0146 (7)	0·4073 (11)
C(1)	0·1951 (18)	0·0799 (10)	0·2766 (14)
C(2)	0·0396 (24)	0·0568 (12)	0·1809 (19)
C(3)	−0·0595 (29)	0·0552 (15)	0·1872 (22)
C(4)	0·0063 (29)	0·0717 (14)	0·2991 (22)
C(5)	0·1603 (27)	0·0979 (13)	0·3999 (21)
C(6)	0·2617 (21)	0·1004 (10)	0·3874 (16)
C(7)	0·2017 (17)	0·1404 (8)	0·1108 (13)
C(8)	0·2041 (23)	0·1220 (12)	0·0336 (18)
C(9)	0·1168 (24)	0·1678 (12)	−0·0692 (19)
C(10)	0·0281 (24)	0·2290 (13)	−0·0967 (21)
C(11)	0·0222 (26)	0·2488 (13)	−0·0227 (19)
C(12)	0·1128 (23)	0·2021 (12)	0·0869 (18)
C(13)	0·5166 (18)	0·1366 (9)	0·3961 (13)
C(14)	0·6588 (21)	0·0974 (10)	0·4709 (16)
C(15)	0·8010 (24)	0·1407 (12)	0·5636 (24)
C(16)	0·7971 (23)	0·2189 (11)	0·5825 (18)
C(17)	0·6532 (27)	0·2564 (14)	0·5081 (21)
C(18)	0·5097 (21)	0·2165 (11)	0·4133 (16)
C(19)	0·3641 (18)	−0·0219 (9)	0·2516 (14)
C(20)	0·3203 (21)	−0·0843 (11)	0·2745 (15)
C(21)	0·3606 (21)	−0·1611 (11)	0·2760 (16)
C(22)	0·4391 (28)	−0·1746 (13)	0·2506 (21)
C(23)	0·4897 (24)	−0·1125 (12)	0·2351 (18)
C(24)	0·4531 (22)	−0·0340 (10)	0·2351 (16)

lines joining the pairs of hydrogen-bonded atoms, it is possible to deduce that the peripheral hydrogen atoms in the strongly hydrogen-bonded pairs of water molecules (the $H_5O_2^+$ ions) lie in positions *trans* to each other. Previous structure determinations involving the $H_5O_2^+$ ion have shown it to have either the *trans* or the *gauche* form and, in two structures, the *cis* form (Williams, 1969; Williams & Peterson, 1971). Although the short O···O hydrogen bonds have poorly established dimensions [and O(1)··· O(1′)=2·35 Å is certainly too short due to the poor location of O(1)] it is clear that they fall into the same category of very short and probably centrally bridged hydrogen bonds as those found in certain acid salts (Speakman, 1967). The OH–Cl⁻ hydrogen bonds are slightly shorter than the average value of 3·12 Å for this type of hydrogen bond (Wallwork, 1962) suggesting that the positive charge of the $H_5O_2^+$ ion resides partly on the peripheral hydrogen atoms.
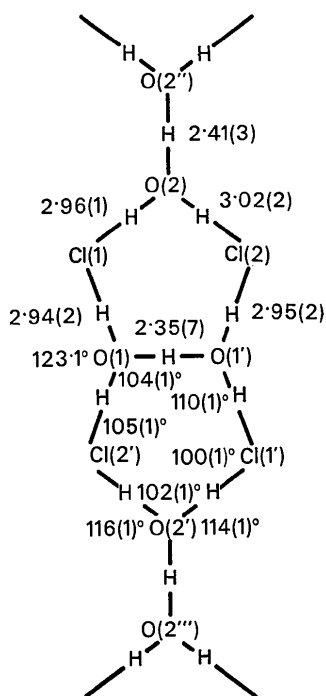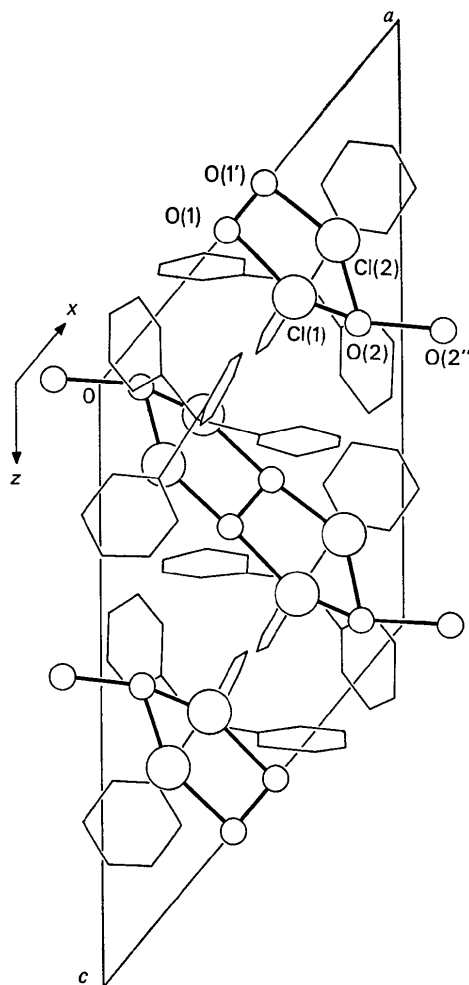
Fig. 1. Distances and angles in the hydrogen bond system (with standard deviations in parenthes). Hydrogen positions have not been determined.

Fig. 2. The structure viewed along the *y* axis.

Computing Centre, University of Nottingham, for computing facilities.

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Crystal structure of tetramethylammonium cadmium chloride.* By. B. MOROSIN, *Sandia Laboratories, Albuquerque, New Mexico* 87115, *U.S.A.*

The crystal structure of tetramethylammonium cadmium chloride, $(CH_3)_4NCdCl_3$, has been refined using the full-matrix least-squares method on 506 Mo $K\alpha$ intensity data. The compound crystallizes in space group $P6_3/m$ with lattice constants $a_0 = 9 \cdot 138$ and $c_0 = 6 \cdot 723$ Å and a structure consisting of infinite linear chains formed from face-shared cadmium-chloride ion octahedra (Cd–Cl separation of $2 \cdot 641$ Å and Cl–Cd–Cl angle of $96 \cdot 05°$ along the chain) and of disordered $[N(CH_3)_4]^+$ ions.

Introduction

Recent low-temperature neutron scattering experiments on tetramethylammonium manganese chloride (TMMC) have shown that the $-MnCl_3^-$ chains magnetically order at low temperature (Birgeneau, 1971). Attempts to grow a dimagnetic isomorphic analog as a host for resonance studies proved successful for only cadmium ions. The crystal structure of tetramethylammonium cadmium chloride (TMCC) proved to be very similar to that for TMMC (Morosin & Graeber, 1967) even to the extent of disorder of the $[N(CH_3)_4]^+$ ions.

Experimental

Colorless, hexagonal prismatic $\{10\bar{1}0\}$ crystals of TMCC were grown either by cooling hot aqueous saturated solutions, prepared with stoichiometric amounts of $N(CH_3)_4Cl$ and $CdCl_2$, or by slow evaporation of similar room-temperature solutions.

The lattice constants for TMCC $[a_0 = 9 \cdot 138$ (1), $c_0 = 6 \cdot 723$ (1) Å] were obtained by least-squares fit of 12 high 2θ values measured on films taken with Cu $K\alpha$ radiation (λ for $K\alpha_1 = 1 \cdot 54050$ Å) using a 115 mm diameter Straumanis loaded, Weissenberg camera. Systematic absences of $00l$ for l odd and the symmetry of the reciprocal lattice as recorded by the precession method indicate the space group to be either $P6_3$ or $P6_3/m$. Comparison of these photographs with those previously taken on TMMC indicated that these compounds are isomorphous. Similarly, the presence of a piezoelectric effect was not detected. There are two formula weights of $N(CH_3)_4CdCl_3$ per cell, yielding a calculated density of $2 \cdot 07$ g.cm^{-3}.

The θ–2θ scan technique and a scintillation counter with pulse-height discrimination were used to measure the Mo $K\alpha$ intensity data on a crystal specimen mounted on $[11\bar{2}0]$. (A Datex automatic-control module was used for setting the angles on the Picker diffractometer and on the

E & A full-circle orienter.) Two symmetry-related sets for both positive and negative values of l were examined for differences that might imply the structure was noncentrosymmetric, or possibly that it consisted of an intimate twinning of two noncentrosymmetric structures (see TMMC). The number of pairs of reflections with the same sign for l which differed by more than 3σ (obtained from counting statistics)* was 64; however, only in five cases did the average value of the positive l differ from that for the negative l by 3σ. On the basis of this comparison of intensities, the presence or absence of the center of symmetry cannot be clearly established. Two data sets were considered for refinement: (1) 506 averaged intensities ($P6_3/m$) of which 116 were measured to be less than 3σ and, thus, considered to be unobserved,† and (2) 941 intensities with both positive and negative l index, of which 117 were correspondingly considered to be unobserved. No absorption corrections were applied to the data set (μMo $K\alpha = 29 \cdot 5$ cm^{-1}: crystal, hexagonal prism $0 \cdot 19 \times 0 \cdot 17 \times 0 \cdot 18$ mm).

Refinement and results

Using the positional parameters determined for TMMC, the above data sets were subjected to full-matrix least-squares refinement using anisotropic thermal parameters. The function, $\sum w(F_o - F_c)^2$, was minimized; weights were assigned from counting statistics or set to zero for unobserved reflections when $F_o < F_c$. Structure factors were calculated with Cd, Cl$^-$, N, and C scattering factors from

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* In the expression for σ $[\sigma = (N_{SC} + K^2 N_B)^{1/2}$, where N_{SC}, N_B, an dK are the total scan count, background counts, and the ratio of the scan to background times, respectively], K rather than K^2 was employed; further, no allowances for instability or other errors, which would be a function of intensity, were made.

† Only one particular measured value of a set needed to be less than 3σ for the intensity to be considered unobserved. For unobserved reflections with positive average values, I_{obs} set equal to the greater of either the average value or $3\sigma_{(ave)}/\sqrt{n}$, where $\sigma_{(ave)}$ is the average σ for n measurements; for negative average values, I_{obs} set to zero. Weights $= n/\sigma^2_{(ave)}$.