

L'atome Fe se projette quasiment au centre du cycle C₅; sa distance au plan moyen du cycle est de 1,74 Å contre 1,70 Å dans les structures précitées ou le cycle pentadiényle est beaucoup moins encombré.

Les atomes de carbone des groupes méthyle Me₅C₅ sont situés au-dessus du plan moyen de C₅, à des distances variant de 0,12 à 0,25 Å, du côté opposé au Fe^{II}, ce qui traduit bien la gêne stérique entre Me₅C₅ d'une part et le reste de l'ensemble organométallique, d'autre part.

Les atomes P(2) et P(3) sont situés hors du plan moyen des quatre cycles phényle à des distances variant de -0,08 à -0,17 Å.

La cohésion cristalline est essentiellement due aux interactions coulombiennes entre l'ion PF₆⁻ et le complexe cationique du Fe^{II}. Les interactions de van der Waals jouent certainement un rôle négligeable; il n'existe, en effet, que très peu de distances interatomiques inférieures à la somme des rayons de van der Waals.

La conformation de l'ensemble cationique, décrite comme étant du type 'tabouret de piano' est également observée pour les deux composés précités, mais dans le cas présent elle est beaucoup plus encombrée stériquement. L'ion PF₆⁻ ne présente pas de caractère particulier.

La présente structure est caractérisée par un encombrement considérable autour de l'atome de fer, entraînant des déformations importantes.

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Structures of the Monohydrate and Dihydrate of (Bidentate Pyrophosphato) *trans*-Diammine *cis*-Diaqua Chromium(III)

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Abstract. (OC-6-32)-Diamminediaqua[pyrophosphato(3-)]chromium(III) monohydrate, [Cr(NH₃)₂(H₂O)₂(HP₂O₇)]·H₂O, *M_r* = 315.1, triclinic, *P* $\bar{1}$, *a* = 7.127 (2), *b* = 8.390 (2), *c* = 9.619 (2) Å, α = 72.14 (2), β = 98.86 (2), γ = 76.98 (3)°, *V* = 517.7 (3) Å³, *Z* = 2, *D_x* = 2.02 g cm⁻³, λ (Cu *K* α) = 1.5418 Å, μ = 129 cm⁻¹, *F*(000) = 322, *T* = 293 K. (OC-6-32)-Diamminediaqua[pyrophosphato(3-)]chromium(III) dihydrate, 0.5{[Cr(NH₃)₂(H₂O)₂(HP₂O₇)]·2H₂O}, *M_r* = 0.5(333.1), monoclinic, *C*2/*m*, *a* = 13.118 (3), *b* = 12.101 (3), *c* = 7.436 (2) Å, β =

105.09 (2)°, *V* = 1139.7 (3) Å³, *Z* = 8, *D_x* = 1.94 g cm⁻³, λ (Cu *K* α) = 1.5418 Å, μ = 118 cm⁻¹, *F*(000) = 684, *T* = 293 K. The structures were solved by the multi-solution technique and refined by the method of least squares to yield a final *R* index of 0.057 for 986 reflections in the monohydrate and a final *R* index of 0.043 for 1030 reflections in the dihydrate. The six-membered chromium pyrophosphate chelate ring is in a boat conformation for the monohydrate with an intramolecular hydrogen bond between an ammonia proton and a pyrophosphate O atom. In the dihydrate, the chelate ring is bisected by the mirror plane resulting in an unusual planar chelate ring conformation which does not permit intramolecular hydrogen bonding.

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Introduction. Nucleotide polyphosphate metal complexes are substrates and cofactors for many enzyme-catalyzed reactions. The nature of the ligands coordinated to the metal polyphosphate can significantly affect enzyme recognition and catalysis. The metal pyrophosphate coordination complexes have been used as models for metal nucleotide substrates to study enzyme reactivity by Cornelius & Cleland (1978), Dunaway-Mariano & Cleland (1980), Pecoraro, Rawlings & Cleland (1984), and Speckhard, Rawlings, Pecoraro & Cleland (1990). Trivalent chromium pyrophosphate complexes with different ratios of water and ammonia provide a large variety of substrates for enzyme binding and reactivity studies.

Here we report the (bidentate pyrophosphato) *trans*-diammine *cis*-diaqua Cr^{III} complex in two crystal forms. These structures are compared to earlier reported structures of tetraaqua(pyrophosphato)chromium(III) (Merritt, Sundaralingam & Dunaway-Mariano, 1981), tetraammine(pyrophosphato)chromium(III) (Haromy, Knight, Dunaway-Mariano & Sundaralingam, 1984), and meridional monoaquatriammine(pyrophosphato)chromium(III) (Haromy, Linck, Cleland & Sundaralingam, 1990).

Experimental. A 100 ml solution containing 10 mM *trans*-[Cr(NH₃)₂(H₂O)₂Br₂]Br (Werner & Klein, 1902) and 10 mM Na₂H₂P₂O₇ was adjusted to pH 3. After the solution was heated for 8 min at 353 K, it was cooled to 277 K and adsorbed on a 1·5 × 20 cm column of Dowex-50W-X2-H⁺, 200–400 mesh. The column was washed with water until 3 bands became apparent and were separated. Unreacted starting material binds tightly to the resin and remains at the top of the column. The resin containing the faster moving major band (*trans* isomer) was transferred to a 1 cm diameter column which was eluted with 0·4 M aniline. The most highly colored fractions were combined and extracted three times with 5 volumes of ether. The slower moving band is presumed to be the *cis* isomer and was isolated in the same fashion, but no crystals have yet been obtained from it. These isomers have the following absorption properties:

trans isomer: $\lambda_{\max} = 562 \text{ nm}$ ($\epsilon = 23$), 405 ($\epsilon = 22$),
isoionic pH 3·17

cis isomer: $\lambda_{\max} = 556 \text{ nm}$ ($\epsilon = 23$), 400 ($\epsilon = 19$),
isoionic pH 3·07

Crystals of the monohydrate were prepared from a 50 mM solution of the *trans* isomer at 298 K, which quickly formed crystals after ether extraction as the solution was cooled to 277 K. Crystals of the dihydrate formed after 3 days of slow evaporation of a 10 mM solution at 277 K.

The data for both structures were collected at 293 K with $\omega/2\theta$ scans on an Enraf-Nonius CAD-4 diffractometer. Monohydrate crystal 0·15 × 0·05 × 0·20 mm and dihydrate crystal 0·10 × 0·05 × 0·15 mm. Cell constants for both structures were determined from 25 well centered reflections using the least-squares technique. The dihydrate data were corrected for decay by measuring three standard reflections at periodic intervals during the data collection with a maximum decay of 15%. No appreciable decay was observed for the monohydrate. An empirical absorption correction (φ curve) was applied to the data sets for both structures with a maximum correction of 20% for the monohydrate and 25% for the dihydrate. Corrections for Lorentz and polarization effects were applied for both structures.

Out of a total of 1065 unique ($R_{\text{int}} = 0·044$) reflections collected up to a 2θ limit of 120°, 986 intensities with $I/\sigma(I) > 2$ were used for the structure analysis of the monohydrate. For the dihydrate, 1030 reflections ($R_{\text{int}} = 0·027$) with $I/\sigma(I) > 2$ out of 1135 reflections up to a 2θ limit of 140° were employed. There were 704 and 1019 multiply observed reflections for the monohydrate and dihydrate, respectively. Both structures were solved by the multi-solution technique and refined by the full-matrix least-squares technique to minimize the differences between F_o and F_c . Anisotropic temperature factors for the non-H atoms and isotropic temperature factors for the H atoms were used in the final refinement of both structures.

Except for H2(W3) of the monohydrate, all of the H atoms were located from difference Fourier maps. H2(W3) was fixed on a vector between the water O atom O(W3) and the hydrogen bond acceptor O3(P1) of a symmetry related molecule. H(O2) of the dihydrate is shared by symmetry related phosphate O atoms, O(2), involved in a short hydrogen bond. The difference Fourier map showed an elongated peak at the center of this hydrogen bond, suggesting that the proton is statistically disordered in a double potential well, being closer to one or the other of the O atoms. Alternatively, the proton can be placed at the center of the hydrogen bond, reflecting a single potential well. In either case the hydrogen bond is symmetric. Both cases were considered in the refinement with no significant differences in the R factor. The proton position at the center of the hydrogen bond is given here, where it lies on a crystallographic twofold axis. The isotropic temperature factor for the proton refined to 14 Å².

A counting statistics weighting scheme was used with the weight of each reflection proportional to $1/[\sigma^2(F) + (0·02F_o)^2]$. For the monohydrate the final $R = 0·057$, $wR = 0·079$ and $S = 2·148$ while for the dihydrate $R = 0·043$, $wR = 0·061$ and $S = 2·492$. The

maximum shift/e.s.d.'s ratios in the final cycles of refinement were less than 0.01 for non-H atoms and less than 0.4 for H atoms. The final $\Delta\rho$ excursions are -0.5 to $+0.6 e \text{ \AA}^{-3}$ for the monohydrate and -0.3 to $+0.4 e \text{ \AA}^{-3}$ for the dihydrate. The scattering factors used for non-H atoms are from Cromer & Waber (1965) while those for H atoms are from Stewart, Davidson & Simpson (1965). Anomalous-scattering components for non-H atoms are from the *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 148–151). Calculations were performed on a MicroVAX II computer using locally developed programs (Rao, Haromy, McAlister & Merritt, 1990, unpublished).

Discussion. Positional parameters for both structures are given in Table 1.* *ORTEP* (Johnson, 1976) drawings are shown in Fig. 1. Fig. 2 gives bond lengths as well as chelate ring bond angles and torsion angles.

The two water ligands are *cis* to each other and opposite the pyrophosphate O atoms in the chromium coordination sphere. The two ammonia ligands are *trans* to each other and *cis* to the coordinated phosphate O atoms. The other two possible geometries for this complex have the ammonia ligands *cis* to each other with the water ligands either *trans* or *cis*. In the *cis* case two enantiomeric screw isomers are possible. The failure of the *cis* isomer to crystallize may result from it being a mixture of these isomers. The dihydrate contains a mirror plane through the Cr atom, both N atoms, and the pyrophosphate bridge O atom. Therefore, these atoms have a multiplicity of one-half and their *y* coordinates were fixed at zero.

Geometry. The distances between the metal and the coordinated water O atoms are 2.011 (8) and 1.990 (6) Å for the monohydrate while for the dihydrate, due to the mirror, this distance has only one value of 1.988 (3) Å. This can be compared to an average Cr–water distance of 1.97 (2) for the tetraqua complex and 1.992 Å for the monoaquatrimmine complex. The average Cr–ammonia distance is 2.04 (1) in the monohydrate and 2.07 (1) Å in the dihydrate, compared to an average distance of 2.07 (1) for the tetraammine complex and 2.06 (1) Å for the monoaquatrimmine complex. The Cr–water coordination bonds are on average 0.04 Å shorter than the Cr–ammonia bonds in the monohydrate, while in the dihydrate they are 0.08 Å shorter. The average Cr–water coordination bond

Table 1. Fractional positional parameters for all atoms of the monohydrate and dihydrate of (bidentate pyrophosphato) *trans*-diammine *cis*-diaqua chromium(III)

$B_{eq} = (4/3)\sum_i\sum_j\beta_{ij}a_i \cdot a_j$					
	x	y	z	B_{eq} or $B(\text{Å}^2)$	
Monohydrate					
Cr	0.2427 (2)	0.1976 (2)	0.7163 (2)	2.66 (6)	
P(1)	0.2145 (3)	0.5494 (3)	0.7720 (2)	2.65 (8)	
P(2)	0.6045 (3)	0.3310 (3)	0.7978 (2)	2.66 (8)	
O1(P1)	0.1284 (7)	0.4387 (7)	0.6977 (6)	3.0 (2)	
O2(P1)	0.1200 (9)	0.7430 (7)	0.6897 (7)	4.1 (2)	
O3(P1)	0.2074 (9)	0.4893 (8)	0.9382 (6)	3.9 (2)	
O(P12)	0.4428 (8)	0.5154 (7)	0.7693 (7)	3.5 (2)	
O1(P2)	0.4939 (8)	0.1945 (7)	0.8297 (7)	3.9 (2)	
O2(P2)	0.6696 (9)	0.3545 (9)	0.6564 (7)	4.8 (3)	
O3(P2)	0.7660 (8)	0.2982 (8)	0.9324 (7)	3.9 (2)	
O(W1)	0.3646 (10)	-0.0502 (9)	0.7326 (11)	8.1 (4)	
O(W2)	-0.0139 (8)	0.1870 (7)	0.6094 (6)	3.5 (2)	
N(1)	0.3154 (13)	0.2866 (11)	0.5143 (9)	4.0 (3)	
N(2)	0.1564 (12)	0.1115 (11)	0.9109 (8)	4.1 (3)	
O(W3)	0.7655 (16)	-0.1764 (16)	0.7918 (14)	12.2 (7)	
H(O3P1)	0.214 (20)	0.590 (19)	0.993 (15)	13 (4)	
H1(W1)	0.492 (15)	-0.070 (13)	0.700 (11)	7 (3)	
H2(W1)	0.278 (12)	-0.105 (11)	0.685 (9)	5 (2)	
H1(W2)	-0.061 (17)	0.218 (16)	0.484 (13)	10 (3)	
H2(W2)	-0.138 (20)	0.236 (19)	0.635 (15)	12 (4)	
H1(N1)	0.293 (16)	0.238 (16)	0.444 (12)	8 (3)	
H2(N1)	0.421 (20)	0.314 (17)	0.516 (13)	10 (3)	
H3(N1)	0.237 (15)	0.387 (14)	0.472 (11)	7 (3)	
H1(N2)	0.203 (10)	0.139 (9)	0.981 (7)	2 (1)	
H2(N2)	0.044 (16)	0.146 (15)	0.911 (11)	8 (3)	
H3(N2)	0.163 (22)	-0.024 (20)	0.931 (14)	13 (4)	
H1(W3)	0.908 (28)	-0.212 (25)	0.782 (18)	18 (6)	
H2(W3)	0.775	-0.280	0.881	18	
Dihydrate					
Cr	0.2230 (1)	0.0000	0.7873 (1)	1.91 (3)	0.50
P	0.3688 (1)	0.1218 (1)	1.1475 (1)	2.06 (3)	
O(1)	0.2968 (2)	0.1138 (2)	0.9520 (3)	2.86 (7)	
O(2)	0.4723 (2)	0.1776 (2)	1.1441 (3)	3.85 (7)	
O(3)	0.3212 (2)	0.1727 (2)	1.2884 (4)	3.59 (7)	
O(4)	0.4024 (3)	0.0000	1.2172 (6)	4.46 (12)	0.50
O(W1)	0.1423 (2)	0.1167 (2)	0.6218 (4)	3.44 (7)	
N(1)	0.3365 (3)	0.0000	0.6375 (6)	3.08 (12)	0.50
N(2)	0.1025 (4)	0.0000	0.9192 (7)	3.72 (14)	0.50
O(W2)	0.1123 (2)	0.1468 (2)	0.2557 (4)	4.03 (8)	
H(O2)	0.500	0.180 (4)	1.000	14 (2)	
H1(W1)	0.164 (4)	0.198 (4)	0.685 (7)	6 (1)	
H2(W1)	0.127 (3)	0.124 (3)	0.491 (6)	4 (1)	
H1(N1)	0.388 (8)	0.000	0.710 (14)	10 (3)	0.50
H2(N1)	0.312 (4)	0.061 (4)	0.551 (7)	5 (1)	
H1(N2)	0.044 (8)	0.000	0.825 (14)	9 (2)	0.50
H2(N2)	0.105 (6)	0.058 (5)	0.972 (9)	8 (2)	
H1(W2)	0.080 (6)	0.207 (6)	0.234 (6)	9 (2)	
H2(W2)	0.168 (4)	0.158 (4)	0.261 (6)	4 (1)	

in the tetraqua complex is 0.08 Å shorter than the average Cr–ammonia coordination bond in the tetraammine complex. Introduction of the water ligands into the coordination sphere shortens the Cr to pyrophosphate oxygen coordination distances from 1.97 (1) in the tetraammine complex to 1.94 (1) (monohydrate) and 1.93 (1) Å (dihydrate). These lengths are comparable to the average Cr to pyrophosphate oxygen coordination distances of 1.94 (1) for the monoaquatrimmine complex and 1.95 (2) Å for the tetraqua complex.

The average angle at the coordinated pyrophosphate O atom of the monohydrate is 129.1 (2) and the value for the dihydrate is 137.6 (2)°. The larger value for the dihydrate is due to the planar chelate ring. The average is 127.9 (4)° for the tetraammine complex, while the same two angles for the tetraqua

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53251 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

complex are very different with values of 125.9 and 132.7°. In the monoaquatriammine complex, which also has a relatively flat chelate ring, this angle has an average value of 136.0(5)°, which is similar to that seen for the dihydrate.

The covalent bond lengths and angles for all four of these complexes (tetraammine, monoqua, diaqua, and tetraqua) are comparable. The P—O bonds to the bridge O atom are the longest for all four complexes; next in order are the P—OH distances with the protonated O atom, followed by the two P—O bonds with the coordinated O atoms, and the P—O bonds carrying the negative charge or double bond are the shortest. The bridge P—O distances are unequal in all four complexes (except for the dihydrate crystal form of the diaqua complex where the mirror requires equality), the bond to the protonated phosphate being shorter by 0.03 to 0.04 Å (Fig. 2).

Chelate ring puckering. The ring puckering amplitude, Q (Cremer & Pople, 1975), of 0.585(6) Å for the monohydrate is comparable to that observed for

the tetraqua and tetraammine complexes (0.58 and 0.62 Å, respectively) but is significantly greater than the degree of puckering observed for the mono-aquatriammine complex which is significantly flatter with a Q of 0.37 Å. θ for the monohydrate is 93.1(8)° while φ is 119.3(6)° indicating that the chelate ring assumes a boat conformation. In contrast, the dihydrate displays a nearly planar chelate ring with $Q = 0.097(5)$ Å. There is a maximum deviation of 0.045(3) Å from a least-squares plane through the six atoms of the chelate ring. A planar chelate ring has not been previously observed for this type of structure. The flattest chelate ring previously observed was in the monoaquatriammine complex ($Q = 0.37$ Å). A more detailed discussion of chelate ring puckering for metal pyrophosphate complexes can be found in Haromy (1982) and Sundaralingam & Haromy (1985).

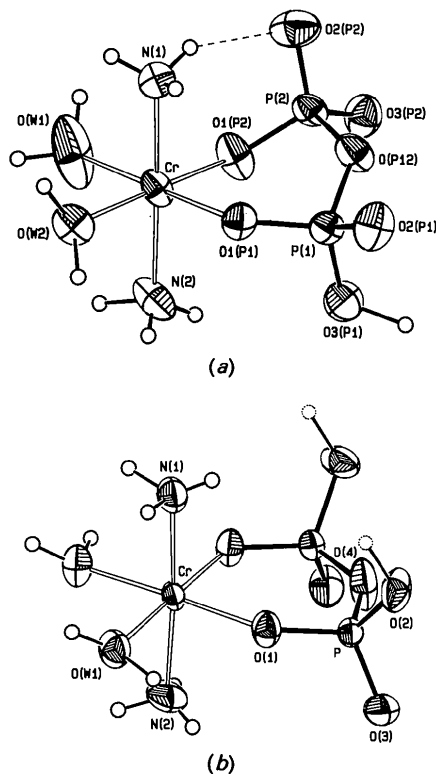


Fig. 1. ORTEP drawings of (a) the monohydrate and (b) the dihydrate with non-H atoms drawn as 50% probability ellipsoids and H atoms drawn as spheres of arbitrary size. The coordination bonds are open while the covalent bonds are solid. They intramolecular hydrogen bond for the monohydrate is shown with a dashed line. Both half protons, one on each O(2) atom of the dihydrate, are shown as dotted circles. The water molecules of hydration are not shown.

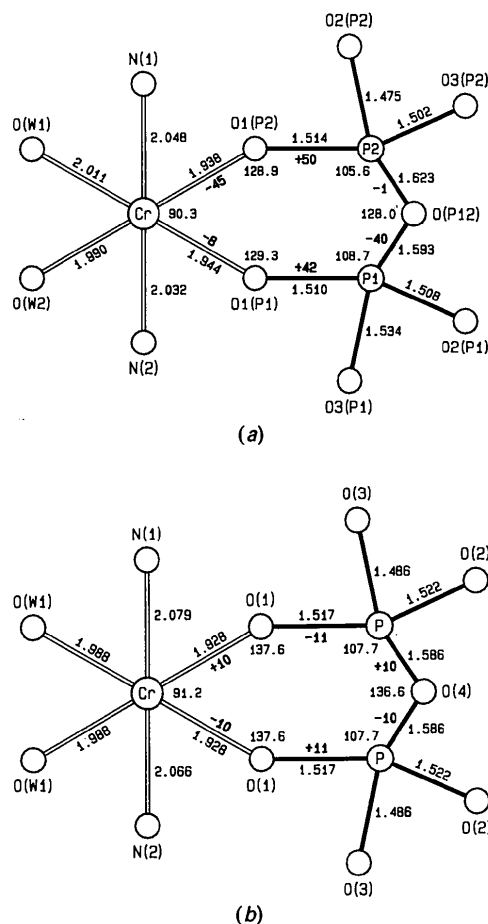


Fig. 2. Bond lengths (Å), ring bond angles (°), and ring torsion angles (°) (signed bold numbers) for (a) the monohydrate and (b) the dihydrate. The estimated standard deviations are 0.006–0.009 Å for bond lengths, 0.3–0.5° for bond angles, and 0.5–0.7° for torsion angles in the monohydrate; and 0.002–0.006 Å for bond lengths, 0.2–0.3° for angles, and 0.3–0.5° for torsion angles in the dihydrate.

Table 2. *Hydrogen-bonding distances for both crystal forms (distances are between participating non-H atoms)*

<i>A—H...B</i>	Sym	Translation			<i>A...B</i>
Monohydrate		<i>x</i>	<i>y</i>	<i>z</i>	
O3(P1)—H(O3P1)...O3(P2)	2	1	1	2	2.491 (9) Å
O(W1)—H1(W1)...O(W3)	1	0	0	0	2.715 (13)
O(W1)—H2(W1)...O2(P1)	1	0	-1	0	2.793 (10)
O(W2)—H1(W2)...O2(P1)	2	0	1	1	2.700 (8)
O(W2)—H2(W2)...O2(P2)	1	-1	0	0	2.558 (9)
N(1)—H1(N1)...O(W3)	2	1	0	1	3.353 (15)
N(1)—H2(N1)...O2(P2)	1	0	0	0	2.937 (12)
N(1)—H3(N1)...O2(P2)	2	1	1	1	2.990 (12)
N(2)—H1(N2)...O(W3)	2	1	0	2	3.064 (15)
N(2)—H2(N2)...O3(P2)	1	-1	0	0	2.941 (11)
N(2)—H3(N2)...O3(P2)	2	1	0	2	3.178 (11)
O(W3)—H1(W3)...O2(P1)	1	1	-1	0	2.865 (13)
O(W3)—H2(W3)...O3(P1)	2	1	0	2	3.018 (14)
Dihydrate		<i>x</i>	<i>y</i>	<i>z</i>	
O(2)—H(O2)...O(2)	6	1	0	2	2.436 (3)
O(W1)—H1(W1)...O(3)	7	0	0	2	2.646 (3)
O(W1)—H2(W1)...O(W2)	1	0	0	0	2.672 (4)
N(1)—H1(N1)...O(4)	1	0	0	-1	3.453 (6)
N(1)—H2(N1)...O(3)	1	0	0	-1	3.298 (4)
N(2)—H1(N2)...O(W2)	5	0	0	1	3.298 (5)
N(2)—H2(N2)...O(W2)	1	0	0	1	3.044 (5)
O(W2)—H1(W2)...O(2)	4	-1	0	-1	2.790 (4)
O(W2)—H2(W2)...O(3)	1	0	0	-1	2.706 (4)

Equivalent positions (crystal symmetry): Monohydrate: (1) *x, y, z*; (2) $-x, -y, -z$. Dihydrate: (1) *x, y, z*; (2) *x, -y, z*; (3) $\frac{1}{2} + x, \frac{1}{2} + y, z$; (4) $\frac{1}{2} + x, \frac{1}{2} - y, z$; (5) $-x, -y, -z$; (6) $-x, y, -z$; (7) $\frac{1}{2} - x, \frac{1}{2} - y, -z$; (8) $\frac{1}{2} - x, \frac{1}{2} + y, -z$.

Hydrogen bonding. All protons in both structures are directed towards potential hydrogen bond acceptors (Table 2). The distances range from 2.436 (3) to 3.018 (14) Å for the O—O hydrogen bonds and from 2.937 (12) to 3.453 (6) Å for the N—O hydrogen bonds. The shortest hydrogen bond in the monohydrate is between O3(P1) and O3(P2), 2.491 (9) Å, and in the dihydrate between symmetry related O(2) atoms, 2.436 (3) Å. The protons involved in both these short hydrogen bonds may be bound to either of the O atoms which they share (Haromy, Knight, Dunaway-Mariano & Sundaralingam, 1983). In the dihydrate, each O(2) atom is hemiprotonated so that one entire molecule, containing two mirror related O(2) atoms, is thus monoprotonated.

O(W3) of the monohydrate and the mirror related waters of hydration in the dihydrate accept three hydrogen bonds and donate two, thus each participates in five hydrogen bonding interactions. These waters of hydration accept one hydrogen bond from an acidic coordinated water with a length of about 2.7 Å and two hydrogen bonds from ammonia ligands with longer distances of 3.0 to 3.3 Å.

As can be seen from the dashed bond in Fig. 1, O2(P2) approaches N(1) in the monohydrate and is stabilized by an intramolecular hydrogen bond of 2.937 (12) Å through H2(N1). In contrast, the N(2)...O3(P1) distance of 3.354 (12) Å for the monohydrate is not sufficiently close for a strong intra-

molecular interaction. The three protons of N(2) make stronger interactions with other acceptors with distances ranging from 2.941 (11) to 3.178 (11) Å. The dihydrate exhibits no intramolecular hydrogen bonding since the nitrogen to phosphate oxygen distances are too long when the chelate ring adopts a planar conformation. The N(1) to O(2) distance is 4.300 (4) Å while the N(2) to O(3) distance is 4.004 (5) Å. Neither the tetraaqua nor the mono-aquatrimmine complexes show intramolecular hydrogen bonding; however, the tetraammine complex has two intramolecular hydrogen bonds, one on each side of the chelate ring, between the axial ammonia ligands and the corresponding axial phosphate O atoms.

Crystal packing. Packing diagrams for both structures are given in Fig. 3. The monohydrate is viewed down the crystallographic *a* axis and the dihydrate down the crystallographic *c* axis. The water of hydration in the monohydrate is seen to fill the empty space between translation related molecules along the *b* axis. In the dihydrate, the chromium pyrophosphate complex is bisected by a unit cell edge (mirror). Each of the mirror-related halves of the chelate rings are associated with one water molecule of hydration; therefore, there are two water

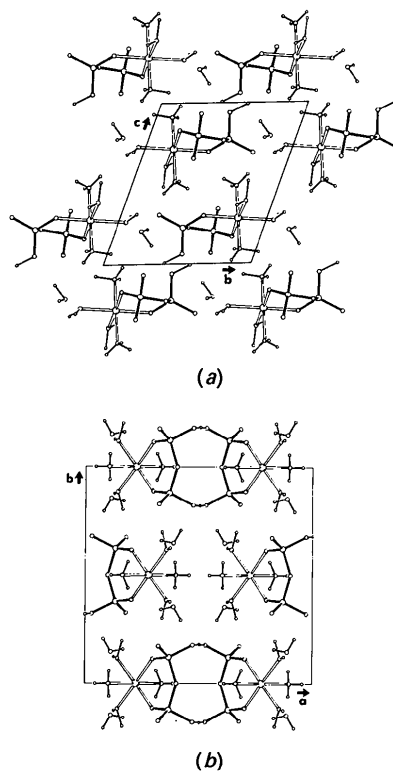


Fig. 3. Packing diagrams for both (a) the monohydrate and (b) the dihydrate. Note the mirror planes in the dihydrate at $y = 0$ and $y = \frac{1}{2}$.

molecules of hydration for each complete chromium pyrophosphate complex. In both crystal structures, the short strong P—O—H···O—P hydrogen bonds link the complexes into hydrogen bonded dimers. The two halves of the dimer are related by a center of symmetry in the monohydrate crystal while in the dihydrate the two halves are related to each other by *2/m* symmetry.

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Redetermination of the Space Group for $[\eta^5\text{-C}_5(\text{CH}_3)_5\text{Cl}_3\text{Ta}[\eta^2\text{-OC}(\text{PEt}_3)\text{Si}(\text{CH}_3)_3]$

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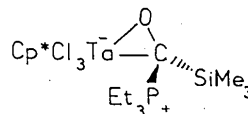
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Abstract. Trichloro(η^5 -cyclopentadienyl)[η^2 -triethyl(trimethylsilylcarbonyl)phosphonio]tantalate, $[\text{TaCl}_3(\text{C}_{10}\text{H}_{15})(\text{C}_3\text{H}_9\text{Si})(\text{C}_6\text{H}_{15}\text{P})]$, $M_r = 641.82$, orthorhombic, *Pca*2₁, $a = 15.820$ (4), $b = 11.314$ (4), $c = 14.809$ (5) Å, $V = 2651$ (1) Å³, $Z = 4$, $D_x = 1.608$ g cm⁻³, $\text{Mo K}\alpha$, $\lambda = 0.71073$ Å, $\mu = 44.8$ cm⁻¹, $F(000) = 1304$, $T = 296$ K, $R = 2.85\%$ for 2428 reflections with $F_o > 3\sigma(F_o)$ and 245 parameters. The structure was originally reported [Arnold, Tilley, Rheingold, Geib & Arif (1989). *J. Am. Chem. Soc.* **111**, 149–164] in the space group *Pcam* ($R = 6.77\%$) as being fully mirror-plane disordered. A re-examination of the structure revealed that an ordered, non-centrosymmetric structure could be smoothly refined by the use of a large damping factor in the least-squares refinement, which minimized the earlier found tendency of the structure to regress toward a disordered, centrosymmetric model. Not only is the *R* factor much improved, but the range of bond parameters for chemically similar portions of the structure, e.g. the differences among the three Ta—Cl distances, has been reduced from

0.14 to 0.07 Å. However, the chemically significant structural features of the earlier report remain unchanged.

Introduction. The structure of the title complex was originally reported (Arnold, Tilley, Rheingold, Geib & Arif, 1989) as fully mirror-plane disordered in the orthorhombic space group *Pcam* ($R = 6.77\%$). We wish now to report that the non-centrosymmetric space group *Pca*2₁ ($R = 2.85\%$) is preferred by the many criteria reported below.



Experimental. Orange-brown crystals cleaved to a cubic shape (0.39 × 0.38 × 0.38 mm) obtained as previously reported (Arnold, Tilley, Rheingold, Geib & Arif, 1989). Nicolet *R3m/μ*, truncated ω (Wyckoff) scans; lattice parameters from 25 reflections, $2\theta < 2\theta$