Fig. 2. Hydrogen-bonding network observed in the structure.

bonded to Co takes part in two hydrogen-bonding interactions. Table 3 lists the hydrogen bonds involved in the crystal structure. Fig. 2 shows the hydrogen-bonding network observed in the structure.

The bonding parameters in the HMT molecule are in good agreement with those found by Becka & Cruickshank (1963) for the HMT molecule. Each of the three N atoms in the HMT molecule is hydrogen bonded to O atoms of three different $Co(H_2O)_6^{2+}$ octahedra. The fourth nitrogen in the HMT molecule forms a hydrogen bond with the oxygen of an independent water molecule. The chloride ion has four short contacts to $O(2)(1-x, 1-y, 1-z)$,

$O(4)(1+x, 1+y, z)$, $O(4)(1-x, 1-y, -z)$ and $O(5)(2-x, 1-y, 1-z)$ which is interesting and rare. The Cl···O contacts range from 3·160 (3) to 3·232 (3) Å. In $AlCl_3.6H_2O$ (Buchanan & Harris, 1968) the chloride ion participates in four hydrogen bonds with Cl···O distances ranging from 3·03 to 3·26 Å. Such an extended hydrogen-bonded network is also observed in $[Co(H_2O)_6](NO_3)_2.2C_6H_{12}N_4.4H_2O$ (Viossat et al., 1981), $CaBr_2.2C_6H_{12}N_4.10H_2O$ (Mazzarella et al., 1967), $MgCr_2O_7.2C_6H_{12}N_4.6H_2O$ (Dahan, 1974) and $CaCr_2O_7.2C_6H_{12}N_4.7H_2O$ (Dahan, 1975).

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Structures of the Meridional and Facial Isomers of Triamminechromium Pyrophosphate Dihydrate

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Abstract. The meridional and facial isomers of triamminechromium pyrophosphate were separated by chromatography on Dowex-50-H$^+$, and crystallized as isoionic species. The meridional isomer crystallized as a monomer $[Cr(HP_2O_7)(NH_3)_3(H_2O)].2H_2O$ but the facial isomer crystallized as a centrosymmetric dimer of $[Cr(HP_2O_7)(NH_3)_3].2H_2O$, in which the remaining water in the coordination sphere of each chromium is replaced by a phosphate oxygen from the other monomer unit. Meridional isomer: monoaquatriammine(pyrophosphato)chromium(III) dihydrate, $M_r = 332·1$, monoclinic, $P2_1/c$,

$a = 7\cdot825$ (2), $b = 10\cdot107$ (3), $c = 15\cdot322$ (5) Å, $\beta = 103\cdot92$ (5)°, $V = 1176$ (1) Å^3, $Z = 4$, $D_x = 1\cdot875$ g cm^{-3} λ(Mo $K\alpha$) $= 0\cdot71073$ Å, $\mu =$ $12\cdot6$ cm^{-1}, $F(000) = 684$, final $R = 0\cdot050$ for 1828 reflections. The most notable difference between this compound and the corresponding tetraammine complex reported previously is a significant shortening of the metal–ligand bond lengths not only for the water ligand but also for the ammonia ligands. The dimer: μ-(pyrophosphato-O,O',O'')-bis[triamminechromium(III)] dihydrate, $M_r = 314\cdot0$, monoclinic, $P2_1/c$, $a = 8\cdot695$ (2), $b = 10\cdot327$ (3), $c = 11\cdot913$ (4) Å, $\beta = 97\cdot81$ (5)°, $V = 1060$ (1) Å^3, $Z = 4$, $D_x = 1\cdot969$ g cm^{-3}, λ(Cu $K\alpha$) $= 1\cdot5418$ Å, $\mu =$ $125\cdot7$ cm^{-1}, $F(000) = 644$, final $R = 0\cdot047$ for 1389 reflections. This structure, which sits on a center of inversion, forms a tricyclic complex involving two Cr atoms. The structure is characterized by reciprocal coordination between the metal ions and anionic O atoms of the pyrophosphate moieties. An eight-membered ring is formed between the two standard six-membered metal(III)–pyrophosphate chelate rings. The ability to distinguish facial from meridional isomers of triamminechromium pyrophosphate provides a key step in the determination of the absolute configurations of triamminechromium complexes of ADP and ATP. Such complexes should prove to be valuable tools for mapping enzyme active sites, since enzymes will show tighter affinity for complexes where water, rather than ammonia, is bound to the protein.

Introduction. Nucleotides in association with metal ions play a key role as substrates and cofactors for many enzyme-catalyzed reactions. The nature of the metal–phosphato coordination can significantly affect the recognition and the interaction of the metal–nucleotide chelate complex with the enzyme. In the case of Mg^{II}, which is the normal metal cofactor *in' vivo*, the various coordination modes rapidly interconvert in solution. In contrast, the corresponding Cr^{III}, Co^{III}, and Rh^{III} coordination complexes are sufficiently stable to permit their isolation and characterization. These trivalent metal complexes have been used to study variations in enzyme reactivity toward substrates with different coordination modes (Cornelius & Cleland, 1978; Dunaway-Mariano & Cleland, 1980; Knight, Ting, Chuang, Dunaway-Mariano, Haromy & Sundaralingam, 1983; Pecoraro, Rawlings & Cleland, 1984).

Previously known inert coordination complexes of nucleotides and polyphosphates have had either all water or all ammonia ligands in coordination positions not occupied by phosphate O atoms and enzymes have shown much tighter binding of complexes containing water than of those containing ammonia (Janson & Cleland, 1974). In a mononu-

clear bidentate triammine complex of ADP or ATP, however, there will be one remaining aqua ligand and it can occupy one of four possible positions, as shown in Fig. 1 for Λ ADP complexes. Since both Λ and Δ chiral isomers are possible, a total of eight isomers should exist for mononuclear bidentate triamminechromium complexes of molecules such as ADP, ATP or tripolyphosphate. Such complexes would be useful probes of the detailed structure of enzyme active sites, since isomers where the aqua ligand faced the enzyme should bind more tightly than those where the aqua ligand faced the solvent and did not interact with the enzyme.

In Fig. 1, isomers in which the water O atom occupies position 1 or 4 will have a facial arrangement of ammonia ligands, while isomers in which the water is in position 2 or 3 will be meridional. Until now pure meridional or facial triamminechromium isomers have not been prepared, but we have discovered that triamminechromium pyrophosphate can be separated into two isomers, and the crystal structures reported here demonstrate that these are indeed meridional and facial, although the facial isomer crystallizes as a dinuclear complex in which coordinated waters are replaced by bridging phosphate O atoms. The structures reported here have laid the foundation for work with triamminechromium complexes of tripolyphosphate and ATP (Speckhard, Rawlings, Pecoraro, & Cleland, 1989).

Experimental. The crystals were prepared as follows: A solution containing 20 mM [Cr(NH$_3$)$_3$(H$_2$O)Cl$_2$]Cl (Werner, 1906) and 20 mM Na$_2$H$_2$P$_2$O$_7$ was heated at 343 K for 10 min. After cooling, this solution was loaded on a $1\cdot6 \times 20$ cm column of Dowex 50-X2 H$^+$ (200–400 mesh) resin at 277 K and eluted with water until two bands were resolved. The resin containing each band was removed and eluted on a second column with $0\cdot3$ M aniline, and the aniline was extracted with ether. Storage at 263 K for
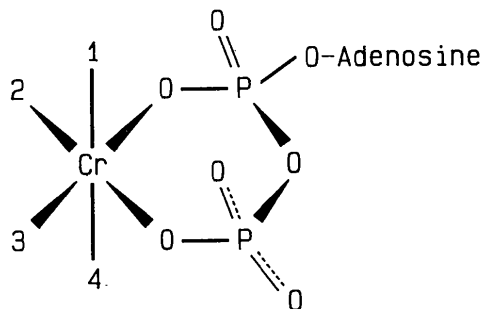

Fig. 1. Chemical structure of monoaquatriamminechromium ADP. One of positions marked 1–4 will be occupied by water while the other three positions are occupied by ammonia. The complex shown has Λ chirality; attachment of adenosine to the other phosphate oxygen gives the Δ isomer.

several days yielded crystals of the meridional isomer, while the facial isomer crystallized after several weeks at 277 K.

X-ray data for the meridional isomer were collected on a Syntex $P3$ diffractometer using Mo $K\alpha$ radiation. Out of a total of 2170 unique reflections collected up to a 2θ limit of $51°$, 1828 reflections with $I/\sigma(I) > 2$ were considered observed and used for the structure analysis. X-ray data for the facial isomer were collected on an Enraf–Nonius CAD-4 diffractometer using Cu $K\alpha$ radiation. Out of a total of 1571 unique reflections collected up to a 2θ limit of $120°$, 1389 reflections with $I/\sigma(I) > 2$ were used for the structure analysis. Data collected for $0 \le h \le 9$; $0 \le k \le 12$; $-18 \le l \le 17$ (meridional) and $0 \le h \le 9$; $0 \le k \le 11$; $-13 \le l \le 12$, at room temperature and with ω–2θ scans and corrected for decay by measuring three standard reflections at periodic intervals during the data collection. The maximum decay was 6% and 15% for the meridional and facial isomers, respectively. A two-parameter empirical absorption correction based on both θ and φ (Haromy, 1982) with a maximum absorption variation of 20% for the meridional isomer and a maximum of 30% for the dimer. Corrections for Lorentz and polarization effects were applied for both structures. There were 87 and 110 multiply observed reflections for the meridional and facial isomers, respectively. The discrepancy from the mean $(\Sigma|F_o - F_c|/\Sigma F_o$, where F_o is the mean structure factor for each unique intensity) for these multiply observed reflections is 0·037 for both structures.

The meridional isomer was solved by the multisolution technique while the facial isomer was solved by the heavy-atom technique. The full-matrix least-squares technique was used for both structures to minimize the differences between F_o and F_c. All of the H atoms were located on difference Fourier maps. 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. A counting statistics weighting scheme was used for both structures with the weight of each reflection proportional to $1/[\sigma^2(F) + (0.03F_o)^2]$. For the meridional isomer the final $R = 0.050$ and $S = 1.566$ while for the dimer $R = 0.047$ and $S = 1.659$. The final weighted R indices are 0·065 for both structures. The maximum shift/e.s.d. ratio for both structures in the final cycle of refinement was less than 0·02 for non-H atoms and less than 0·40 for H atoms. The final $\Delta\rho$ excursions are -0.5 to $+0.6$ e Å^{-3} for the meridional isomer and -0.3 to $+0.4$ e Å^{-3} for the facial isomer. The scattering factors used for non-H atoms are from Cromer & Waber (1965) while those for hydrogen are from Stewart, Davidson & Simpson (1965). Anomalous-scattering components for non-H atoms are from

International Tables for X-ray Crystallography (1974). Calculations were performed on PDP-11/35 and MicroVAX-II computers using locally developed programs (Rao, Haromy, McAlister & Merritt, unpublished).

Discussion. Triamminechromium pyrophosphate as prepared in this work consists of 80% meridional and 20% facial isomers which can be separated by chromatography on Dowex-50-H$^+$. The predominance of the meridional isomer presumably reflects the meridional arrangement of ammine ligands in $Cr(NH_3)_3(O_2)_2$ (McLaren & Helmholtz, 1959), which is the precursor of $[Cr(NH_3)_3(H_2O)Cl_2]Cl$. A similar ratio of meridional isomer to facial isomer is seen for triamminechromium tripolyphosphate complexes (Speckhard *et al.*, 1989). The spectral characteristics of the two isomers at isoionic pH (3·5) are: meridional isomer: $\lambda_{max} = 394$ nm, $\varepsilon = 27$; $\lambda_{max} = 536$ nm, $\varepsilon = 31$; facial isomer: $\lambda_{max} = 393$ nm, $\varepsilon = 23$; $\lambda_{max} = 543$ nm, $\varepsilon = 31$. These isomers are photochemically labile, and care must be taken to protect them from prolonged exposure to light. The facial isomer seems to be more light sensitive.

The positional parameters for both structures are given in Table 1.* The isotropic temperature factors (B) are given for the H atoms and equivalent isotropic temperature factors (B_{eq}) are provided for the non-H atoms. *ORTEP* (Johnson, 1976) drawings of both structures are shown in Fig. 2. Bond distances and chelate-ring bond angles for both structures are provided in Fig. 3. The dimer structure is centrosymmetric with the two halves of the dimer related by a center of inversion at the origin. Only the asymmetric part of the dimer molecule is shown in Fig. 3.

Geometry. The structure of the meridional compound is a hybrid between the previously reported crystal structures of tetraammine(pyrophosphato)-chromium(III) (Haromy, Knight, Dunaway-Mariano & Sundaralingam, 1984) and tetraaqua(pyrophosphato)chromium(III) (Merritt, Sundaralingam, & Dunaway-Mariano, 1981). The substitution of an ammonia ligand in the tetraammine complex with water results in a shortening of the remaining Cr—ammonia bonds from an average value of 2·072 (9) Å ($\sigma = 0.002$ Å for the individual distances) in the tetraammine complex to 2·056 (2) Å in the present structure. Concomitantly, the Cr—water distance of 1·993 (3) Å is lengthened compared to the average Cr—water coordination distance of 1·97 (2) Å ($\sigma = 0.003$ Å for the individual distances)

Table 1. *Fractional positional parameters for* (a) *meridional monoaquatriammine(pyrophosphato)-chromium*(III) *dihydrate and* (b) *the* α,β,β'-*tridentate triammine(pyrophosphato)chromium*(III)*dihydrate dimer*

Values are multiplied by 10^4 for non-H atoms and 10^3 for H atoms.

$$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq} or B
(a)				
Cr	3441 (1)	1899 (1)	681 (1)	1·88 (2)
P(1)	6920 (1)	2786 (1)	63 (1)	2·00 (2)
P(2)	6446 (1)	3883 (1)	1742 (1)	2·23 (2)
O1(P1)	5193 (4)	2039 (3)	−28 (2)	2·65 (6)
O2(P1)	8385 (4)	1925 (3)	−68 (2)	3·00 (6)
O3(P1)	6678 (4)	4029 (3)	−494 (2)	3·21 (9)
O(P12)	7558 (4)	3251 (3)	1103 (2)	2·96 (6)
O1(P2)	4668 (4)	3195 (3)	1542 (2)	2·69 (6)
O2(P2)	7528 (4)	3742 (3)	2670 (2)	3·36 (8)
O3(P2)	6234 (4)	5362 (3)	1506 (2)	3·46 (9)
O(W1)	2082 (5)	601 (3)	−195 (2)	3·81 (9)
N(1)	1652 (5)	1726 (4)	1464 (3)	3·09 (10)
N(2)	4791 (5)	331 (4)	1377 (3)	2·94 (10)
N(3)	1918 (5)	3327 (4)	−90 (3)	3·13 (10)
O(W2)	1122 (5)	1054 (4)	−1985 (3)	5·59 (14)
O(W3)	8053 (7)	1012 (4)	2984 (3)	6·22 (12)
H(O3P2)	550 (6)	557 (5)	116 (3)	3·7 (11)
H1(W1)	189 (6)	−28 (5)	7 (3)	3·9 (11)
H2(W1)	175 (7)	70 (5)	−87 (3)	4·3 (12)
H1(N1)	192 (7)	227 (5)	201 (4)	4·3 (12)
H2(N1)	147 (7)	92 (5)	162 (3)	4·0 (12)
H3(N1)	79 (7)	195 (5)	117 (4)	4·8 (13)
H1(N2)	406 (6)	−19 (6)	160 (3)	4·3 (12)
H2(N2)	510 (8)	−15 (6)	95 (4)	5·8 (14)
H3(N2)	552 (6)	58 (5)	182 (3)	3·7 (11)
H1(N3)	216 (7)	415 (5)	13 (4)	5·2 (13)
H2(N3)	232 (7)	330 (6)	−64 (4)	5·3 (13)
H3(N3)	63 (7)	319 (5)	−21 (4)	5·0 (13)
H1(W2)	123 (7)	20 (5)	−233 (3)	4·8 (12)
H2(W2)	−11 (7)	119 (6)	−207 (4)	5·2 (13)
H1(W3)	795 (7)	194 (6)	287 (4)	5·1 (13)
H2(W3)	768 (7)	96 (6)	350 (4)	5·4 (13)
(b)				
Cr	1165 (1)	−1217 (1)	−1532 (1)	2·17 (2)
P(1)	2891 (1)	1458 (1)	−821 (1)	2·58 (3)
P(2)	1998 (1)	−143 (1)	1020 (1)	2·49 (3)
O1(P1)	2310 (4)	399 (4)	−1623 (3)	3·88 (9)
O2(P1)	2255 (7)	2723 (4)	−1138 (4)	7·45 (14)
O3(P1)	4620 (4)	1526 (6)	−625 (4)	6·47 (14)
O(P12)	2427 (5)	1137 (4)	394 (3)	4·34 (9)
O1(P2)	1378 (4)	−1106 (3)	114 (3)	2·96 (7)
O2(P2)	819 (4)	270 (3)	1757 (2)	3·14 (8)
O3(P2)	3439 (4)	−637 (5)	1740 (3)	4·52 (10)
N(1)	−10 (5)	−2925 (4)	−1430 (3)	3·55 (10)
N(2)	923 (5)	−1415 (4)	−3253 (3)	3·53 (11)
N(3)	3226 (5)	−2205 (5)	−1445 (4)	4·24 (12)
O(W1)	4706 (5)	5864 (5)	1618 (4)	6·51 (14)
O(W2)	2374 (6)	5120 (5)	−105 (5)	7·27 (15)
H(O3P2)	431 (9)	−115 (7)	126 (7)	11·3 (22)
H1(N1)	−75 (6)	−285 (6)	−119 (5)	5·6 (13)
H2(N1)	60 (6)	−351 (5)	−106 (5)	4·3 (12)
H3(N1)	−35 (6)	−307 (7)	−213 (5)	7·0 (16)
H1(N2)	6 (5)	−162 (5)	−345 (4)	4·3 (12)
H2(N2)	134 (5)	−201 (5)	−342 (4)	3·3 (10)
H3(N2)	123 (6)	−86 (5)	−355 (4)	3·9 (11)
H1(N3)	368 (7)	−198 (6)	−190 (6)	7·6 (16)
H2(N3)	366 (6)	−212 (5)	−92 (4)	5·1 (13)
H3(N3)	315 (6)	−299 (6)	−159 (5)	5·9 (14)
H1(W1)	536 (6)	518 (6)	201 (5)	6·5 (15)
H2(W1)	539 (7)	671 (8)	142 (6)	9·6 (19)
H1(W2)	247 (6)	445 (6)	−30 (5)	5·8 (14)
H2(W2)	335 (6)	517 (6)	34 (5)	6·0 (14)

in the tetraaqua complex (Merritt *et al.*, 1981). Thus the coordinate bond lengths represent a hybrid between the values observed for the tetraammine and tetraaqua complexes. The overall shortening of the metal–ligand bond lengths compared to the tetraam-

mine complex can be attributed both to the electronegativity of the O atom as well as to the reduction of steric interactions between the ligand protons since the water molecule has only two protons compared to the three protons found on the ammonia molecule which it replaced. The water ligand also results in a significant shortening of the chromium–pyrophosphate coordination distances from 1·968 (4) Å in the tetraammine complex to 1·945 (3) Å in the present complex. The average angle of 127·9 (4)° at the coordinated pyrophosphate O atoms of the tetraammine complex is significantly smaller than the average angle of 136·0 (5)° in the present structure. The covalent bond lengths and angles for tetraammine, tetraaqua, and the meridional isomer are comparable, as expected.
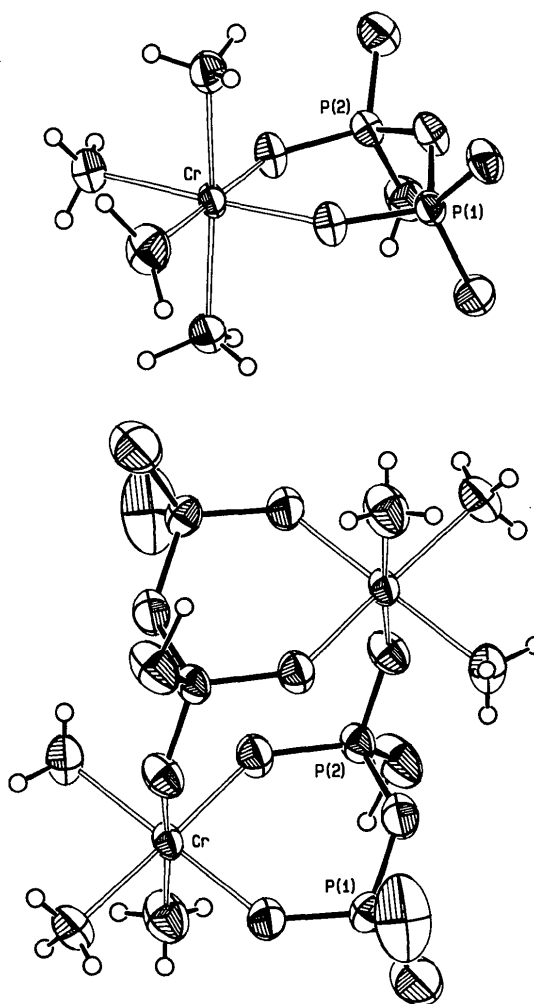

Fig. 2. *ORTEP* drawings of the meridional complex (top) and the dimeric complex (bottom) with non-H atoms drawn as 50% probability ellipsoids and H atoms drawn as spheres of arbitrary size. The coordination bonds are open while the covalent bonds are solid.

In the dimer, each Cr atom is coordinated through oxygen to both P(1) and P(2) of one pyrophosphate moiety to yield the standard metal–pyrophosphate complex, as well as to P(2) of the inversion-related pyrophosphate molecule. The average Cr—ammonia coordination length of 2·048 (4) Å in the dimer is slightly less than the corresponding average of 2·056 (2) Å for the meridional complex. The average coordination distance to the O atoms of the primary pyrophosphate group of 1·951 (3) Å is also close to the value seen for the meridional complex. In contrast, the coordination distance of 1·969 Å to the O atom O2(P2) of the secondary phosphate group is substantially longer. The covalent bonds in the pyro-
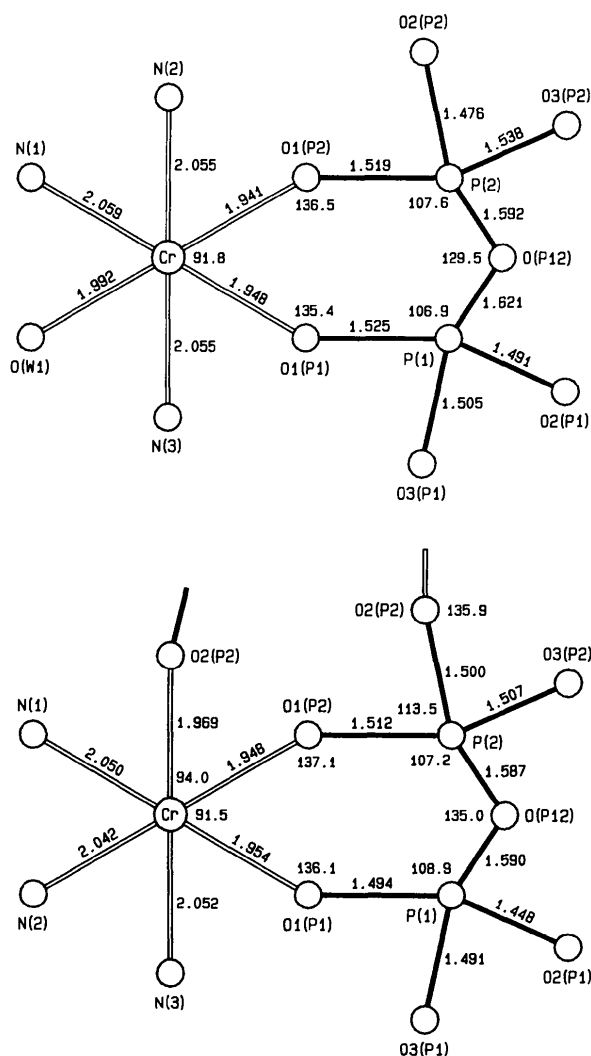
phosphate moiety of the dimer tend to be shorter than the corresponding bonds in the meridional complex. The P(2)—O2(P2) bond is longer in the dimer due to the ligation of O2(P2) to the second Cr atom. The six-membered chelate ring bond angles are comparable for the dimer and meridional complex except for the angle at the bridge O atom which is significantly wider for the dimer (135·0°) than in the meridional complex (129·5°).

Chelate ring puckering. The six-membered chelate ring for the meridional complex is significantly flatter than the corresponding rings observed for any of the previously reported metal(III)–pyrophosphate complexes (Haromy, 1982; Sundaralingam & Haromy, 1985; Shorter, Haromy, Scalzo-Brush, Knight, Dunaway-Mariano & Sundaralingam, 1987). Only the pyrophosphate bridge O atom O(P12) displays any significant pucker with a deviation of 0·465 Å from a least-squares plane through the other five atoms (r.m.s. deviation of 0·04 Å). The dimer complex exhibits not only the six-membered chelate ring typical for a metal pyrophosphate complex, but also an eight-membered ring resulting from the dimerization. The six-membered chelate ring is even flatter in the facial dimer than in the meridional monomer; the O(P12) atom deviates by only 0·272 Å from a least-squares plane through the other five atoms (r.m.s. deviation of 0·08 Å). The ring-puckering parameters (Cremer & Pople, 1975) for those two structures are compared with those observed for the six-membered rings of previously reported bidentate metal–pyrophosphate chelate complexes in Table 2.

In the case of the dimer, the constraints of dimer formation have forced the six-membered ring into a relatively planar conformation to facilitate the stacking between the symmetry-related rings. The six-membered rings lie in nearly parallel planes with an interplanar stacking separation between these rings of 3·08 Å. The eight-membered ring resulting from dimer formation adopts a sofa-like conformation. Since the eight-membered ring contains an inversion center, there are only four independent bond lengths and bond angles for this ring (Fig. 3). The Cremer–Pople puckering parameters for the eight-membered Cr—O1(P2)—P(2)—O2(P2)—Cr— O1(P2)—P(2)—O(P2) ring are $q_3 = 4·13$ (2) Å, $\varphi_3 = 323°$, with $q_2 = q_4 = 0$ due to the symmetry constraints imposed upon the ring.

Hydrogen bonding. All protons in both structures are directed towards potential hydrogen-bond acceptors (Table 3). The distances between the interacting non-H atoms range from 2·505 to 3·366 Å in the meridional complex and from 2·463 to 3·333 Å in the dimer. The acceptor atoms O2(P2) of the meridional isomer and O2(P1) of the dimer appear to be involved in four hydrogen bonds with one of them being significantly weaker than the other three in

Fig. 3. Bond lengths (Å) and ring bond angles (°) for the meridional complex (top) and the dimeric complex (bottom). The incomplete bonds for the dimer connect to the symmetry-related half which has identical bond lengths and angles. The e.s.d.'s are 0·004 Å for the bond lengths and 0·3° for the bond angles in both structures.

Table 2. *Cremer–Pople* (1975) *ring-puckering parameters for the six-membered chelate ring of all reported crystal structures involving metal–pyrophosphate chelate complexes*

	Q (Å)	θ (°)	φ (°)	Reference
Meridional isomer	0·37	71	169	(1)
Facial dimeric isomer	0·23	100	10	(1)
Tetraammine-chromium-PP	0·62	89	104	(2)
Tetraaqua-chromium-PP	0·58	96	307	(3)
Tetraaqua-rhodium-PP	0·76	91	83	(4)
Tetraammine-cobalt-PP	0·62	87	108	(5)
β,γ-Tetraammine-cobalt-PPP	0·50	96	68	(5)

References: (1) this paper; (2) Haromy, Knight, Dunaway-Mariano & Sundaralingam (1984); (3) Merritt, Sundaralingam & Dunaway-Mariano (1981); (4) Shorter, Haromy, Scalzo-Brush, Knight, Dunaway-Mariano & Sundaralingam (1987); (5) Merritt & Sundaralingam (1980).

Table 3. *Potential hydrogen-bonding interactions in the crystal structures*

E.s.d.'s are 0·05 Å for A—H, H···B, 0·005 Å for A···B, and 4° for A—H···B.

(a) The meridional isomer

	Sym.	Translation			Distance (Å)			Angle (°)
A—H···B	code	x	y	z	A—H	H···B	A···B	A—H···B
O3(P2)—H(O3P2)···O3(P1)	3	1	1	0	0·71	1·81	2·505	165
O(W1)—H1(W1)···O2(P1)	3	1	0	0	1·00	1·68	2·624	155
O(W1)—H2(W1)···O(W2)	1	0	0	0	1·01	1·70	2·703	173
N(1)—H1(N1)···O(W2)	2	0	0	0	0·98	2·47	3·366	152
N(1)—H2(N1)···O2(P2)	4	1	−1	0	0·87	2·50	3·295	153
N(1)—H3(N1)···O2(P1)	1	−1	0	0	0·75	2·33	3·033	157
N(2)—H1(N2)···O2(P2)	4	1	−1	0	0·90	2·15	3·046	171
N(2)—H2(N2)···O1(P1)	3	1	0	0	0·89	2·35	3·166	151
N(2)—H3(N2)···O(W3)	1	0	0	0	0·81	2·37	3·167	168
N(3)—H1(N3)···O3(P1)	3	1	1	0	0·90	2·07	2·945	164
N(3)—H2(N3)···O3(P2)	3	1	1	0	0·97	2·37	3·172	141
N(3)—H3(N3)···O2(P1)	1	−1	0	0	0·99	2·23	3·114	149
O(W2)—H1(W2)···O(W3)	3	1	0	0	1·03	1·76	2·756	163
O(W2)—H2(W2)···O2(P2)	4	−1	0	−1	0·95	1·80	2·741	172
O(W3)—H1(W3)···O2(P2)	1	0	0	0	0·95	1·86	2·814	174
O(W3)—H2(W3)···O3(P1)	2	0	0	0	0·91	1·89	2·794	173

(b) The dimer

	Sym.	Translation			Distance (Å)			Angle (°)
A—H···B	code	x	y	z	A—H	H···B	A···B	A—H···B
O3(P2)—H(O3P2)···O3(P1)	3	1	0	0	1·14	1·33	2·463	169
N(1)—H1(N1)···O(P12)	3	0	0	0	0·74	2·56	3·171	142
N(1)—H2(N1)···O(W2)	1	0	−1	0	0·88	2·28	3·158	174
N(1)—H3(N1)···O1(P1)	4	0	−1	−1	0·86	2·63	3·333	140
N(1)—H3(N1)···O2(P1)	4	0	−1	−1	0·86	2·60	3·333	145
N(2)—H1(N2)···O2(P1)	4	0	−1	−1	0·78	2·12	2·899	175
N(2)—H2(N2)···O1(P2)	2	0	−1	−1	0·75	2·62	3·272	146
N(2)—H3(N2)···O(W2)	2	0	0	−1	0·74	2·35	3·001	148
N(3)—H1(N3)···O(W1)	2	0	0	−1	0·75	2·38	3·116	167
N(3)—H2(N3)···O3(P1)	3	1	0	0	0·69	2·29	2·970	168
N(3)—H3(N3)···O3(P2)	2	0	−1	−1	0·83	2·48	3·128	135
O(W1)—H1(W1)···O3(P2)	4	1	0	0	0·98	1·90	2·823	156
O(W1)—H2(W1)···O2(P1)	3	1	1	0	1·10	2·20	3·139	142
O(W1)—H2(W1)···O3(P1)	3	1	1	0	1·10	2·05	3·033	147
O(W2)—H1(W2)···O2(P1)	1	0	0	0	0·74	2·04	2·760	165
O(W2)—H2(W2)···O(W1)	1	0	0	0	0·94	1·93	2·789	151

Symmetry code: (1) x, y, z; (2) $x, \frac{1}{2} - y, \frac{1}{2} + z$; (3) $-x, -y, -z$; (4) $-x, \frac{1}{2} + y, \frac{1}{2} - z$.

both cases. These weak interactions are characterized by N to O distances greater than 3·25 Å. The shortest hydrogen bond is between O3(P2) and O3(P1) of the dimer. As is commonly found with short hydrogen bonds (Haromy, Knight, Dunaway-Mariano & Sundaralingam, 1983), the proton H(O3P2) appears to be disordered and may be bound to either of the two O atoms at a given time.

The difference Fourier synthesis indicates that the proton is bound with a slight preference to O2(P2). Unlike the meridional complex, the dimer complex has two pairs of bifurcated (or 'three-center') hydrogen-bonding interactions (Jeffrey & Mitra, 1984). One pair involves asymmetric bonds from
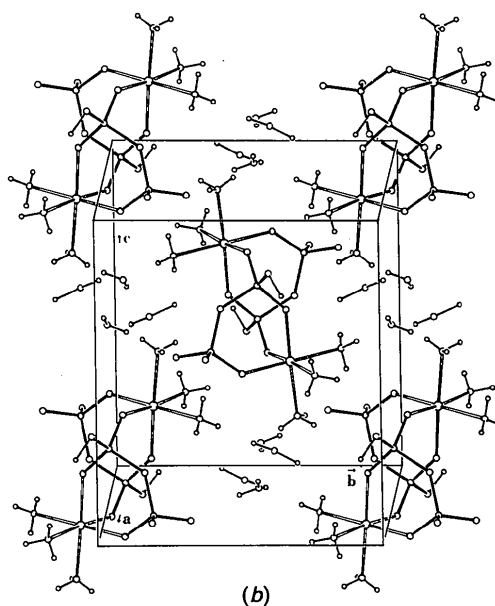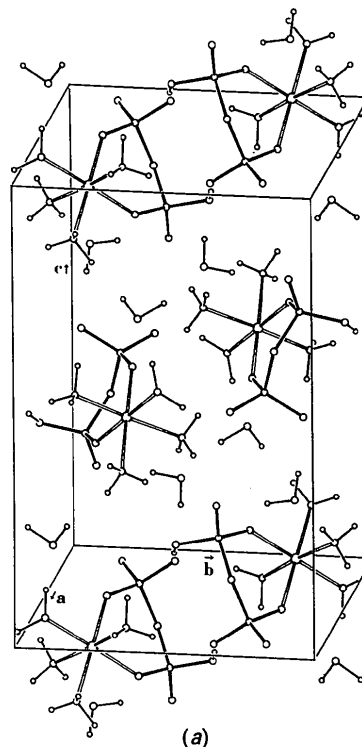
(a)

(b)

Fig. 4. Packing diagrams of both (a) meridional and (b) facial isomers. Both structures are viewed approximately down the a axis with the b axis horizontal and the c axis vertical.

H2(W1) to both O2(P1) and O3(P1) of another symmetry-related molecule with O to O distances of 3·139 and 3·033 Å, respectively. The second pair involves weaker but symmetric hydrogen bonds between H3(N1) and both O1(P1) and O2(P1) of a neighboring phosphate with equal N to O distances of 3·333 Å.

The relatively flat six-membered chelate rings in both structures result in an increased distance between the ammonia ligands on the Cr atom and the phosphate anionic O atoms when compared to the distance for a more sharply puckered chelate ring. This increased distance prevents the formation of any intramolecular hydrogen bonds between the metal ligands and the pyrophosphate O atoms of the type previously observed for several metal-pyrophosphate chelate complexes (Sundaralingam & Haromy, 1985).

Crystal packing. Packing diagrams of both structures are shown in Fig. 4. In both structures, water molecules fill the void between symmetry-related molecules in both the **b** and **c** directions. The centrosymmetric facial dimer complexes sit at the corners and at the center of the unit cell.

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Structure of Disodium Triaquatri-μ-sulfato-thorate(IV) Trihydrate

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Abstract. $Na_2[Th(SO_4)_3(H_2O)_3].3H_2O$, $M_r = 674.290$, monoclinic, $P2_1/c$, $a = 5.567$ (2), $b = 16.81$ (2), $c = 15.76$ (2) Å, $\beta = 91.925$ (4)°, $V = 1474.0$ Å^3, $Z = 4$, $D_m = 2.99$, $D_x = 3.036$ g cm^{-3}, Mo $K\alpha$ radiation (graphite monochromator, $\lambda = 0.71069$ Å), $\mu = 129.25$ cm^{-1}, $F(000) = 1264$, room temperature, final $R = 0.043$ for 2618 unique observed X-ray reflexions.

The thorium is nine-coordinate; all the three sulfates are bidentate and bridging and link the Th atoms into infinite chains parallel to [100]. Three of the six water molecules are coordinated to the thorium. The thorium coordination polyhedron is a slightly distorted tricapped trigonal prism (3/3/3) (idealized symmetry D_{3h}) with $\theta = 46.8°$ (angle between princi-