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Structure of Bidentate Tetraammine(pyrophosphato)chromium(III) Dihydrate, $[Cr(NH_3)_4HP_2O_7].2H_2O$

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Abstract. $M_r = 331{\cdot}1$, monoclinic, $P2_1/c$, $a = 7{\cdot}491\ (1)$, $b = 13{\cdot}840\ (1)$, $c = 11{\cdot}554\ (1)$ Å, $\beta = 93{\cdot}39\ (1)°$, $Z = 4$, $D_x = 1{\cdot}839$ g cm^{-3}, $\lambda(\text{Cu } K\alpha) = 1{\cdot}5418$ Å, $\mu(\text{Cu } K\alpha) = 111{\cdot}2$ cm^{-1}, $F(000) = 684$, room temperature. $R = 0{\cdot}028$ for 2429 observed reflections. The structure has a boat/twist-boat chelate-ring conformation and exhibits two intramolecular hydrogen bonds between the axial ammonia ligands and phosphate O atoms.

Introduction. Tetraammine(pyrophosphato)chromium(III) is one of a series of metal polyphosphate coordination complexes which has been employed to advance our understanding of the binding of polyphosphate substrates to enzymes. Of the trivalent metal M^{III} polyphosphate complexes tested thus far, only those having a bidentate chelate-ring structure (such as β,γ-bidentate M^{III}ATP and P^1,P^2-bidentate M^{III}PP) have shown reactivity with enzymes for which the corresponding Mg^{II} complexes are normal substrates. The β,γ-bidentate chromium tetraaqua ATP $[Cr(H_2O)_4ATP]$ complex can be separated into four stereoisomers on cycloheptaamylose columns while the corresponding β,γ-bidentate cobalt tetraammine $[Co(NH_3)_4ATP]$ complex can be separated into only two stereoisomers (Dunaway-Mariano & Cleland, 1980). The four $Cr(H_2O)_4ATP$ conformers, which arise from two stable conformational states for each of the two P-β screw-sense isomers, are thought to be stabilized in solution by intramolecular hydrogen bonds between the water ligands and phosphate O atoms (Dunaway-Mariano & Cleland, 1980). The corresponding intramolecularly hydrogen-bonded states between the ammonia ligands (in contrast to the water ligands) and phosphate O atoms of $Co(NH_3)_4ATP$ apparently interchange rapidly since they cannot be observed within the NMR time scale (Cornelius, Hart & Cleland, 1977). Because the Cr^{III} complexes are not amenable to NMR spectral analysis and since the M^{III}ATP complexes have yet to be obtained in the crystalline form for X-ray analysis, we have studied the corresponding metal–polyphosphate chelate complexes which serve as models of the M^{III}ATP complexes. The structure of the $Cr(NH_3)_4PP$ complex is compared with the X-ray structures of the $Co(NH_3)_4PP$ (Merritt & Sundaralingam, 1980) and the $Cr(H_2O)_4PP$ complexes (Merritt, Sundaralingam & Dunaway-Mariano, 1981).

Experimental. A 200 ml sample of 20 mM $Na_4P_2O_7$ was adjusted to pH 3 with HCl and added to 200 ml of 20 mM $[Cr(NH_3)_4(H_2O)Cl]Cl_2$ (Pfeiffer, 1905). The solution was heated at 353 K for 10 min, cooled to 277 K and then loaded onto a (4 × 50 cm) Dowex-50-X2 (H^+, 50–100 mesh) column. The column was washed with H_2O until a red band had focused below the Na^+ band. The resin of the red band was transferred to a (2 × 10 cm) 'empty' column, 1 cm of fresh resin was layered on top of the resin bed, and the column was eluted slowly at 277 K with 0·3 M aniline. The eluate was immediately extracted three times with diethyl ether to remove the aniline. Crystals of the title compound appeared after standing at 277 K for 12 h.

Enraf-Nonius CAD-4 diffractometer, rectangular-shaped crystal (0·08 × 0·10 × 0·5 mm), unit-cell parameters by a least-squares algorithm using 25 automatically centered reflections, 2529 unique reflections, $2\theta_{max} = 155°$, 2429 with $I > 2\sigma(I)$ used for structure analysis; four reflections monitored every 2 h during data collection showed 12% decay. Corrections for X-ray absorption were made by using a two-parameter empirical absorption correction based on both φ and θ (Haromy, 1982) and corrections for

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Lorentz–polarization effects were applied. The discrepancy from the mean $(\sum|F_o-\bar{F}_o|/\sum\bar{F}_o)$ for 1770 multiply observed (or symmetry-related) reflections is 0·014 where $\bar{F}_o$ is the mean structure factor for each unique intensity.

Although the chromium structure turned out to be isomorphous with the crystals of the corresponding cobalt complex (Merritt & Sundaralingam, 1980), it was solved independently by the heavy-atom technique. All H atoms from difference Fourier syntheses, refinement on F by full-matrix least-squares technique to a final R of 0·028 and R_w of 0·041 using anisotropic temperature factors for the nonhydrogen atoms and isotropic temperature factors for the H atoms, counting-statistics weighting scheme employed with $w \propto 1/[\sigma^2(F)+(0\cdot01F_o)^2]$, $(\Delta/\sigma)_{\max} = 0\cdot03$ for nonhydrogen atoms and 0·12 for H atoms, final $\Delta\rho$ excursions −0·13 to 0·10 e Å^{-3}, atomic scattering factors for nonhydrogen atoms from Cromer & Waber (1965) and for H from Stewart, Davidson & Simpson (1965), anomalous-scattering components for nonhydrogen atoms from *International Tables for X-ray Crystallography* (1974), all calculations performed on a PDP11/35 computer using locally developed programs (Rao, Haromy, McAlister & Merritt, unpublished).

Discussion. The final positional parameters are presented in Table 1.* An *ORTEP* diagram (Johnson, 1976) is given in Fig. 1. Bond lengths, bond angles, and ring torsion angles are given in Fig. 2.

The volume of 1196 (1) Å^3 for the chromium complex is 51 Å^3 greater than the volume for the isomorphous cobalt complex. The increased unit-cell volume can be attributed to the increase in the average Cr—N coordination bond distance of 2·07 (1) Å which is 0·13 Å longer than the average Co—N coordination bond distance of 1·94 (1) Å. The average Cr—O coordination bond distance of 1·968 (5) Å is only 0·03 Å longer than the average Co—O distance of 1·938 (2) Å. The covalent bond lengths of the pyrophosphate moiety are comparable for both structures with a maximum deviation of 0·005 Å. The metal to bridge oxygen distance [Cr—O(P12)] of 3·476 (1) Å is 0·051 Å greater than the corresponding Co—O(P12) distance.

The isomorphous chromium and cobalt complexes assume boat/twist-boat chelate-ring conformations with metal—O1(P1)—P(1)—O(P12)—P(2)—O1(P2) ring-puckering parameters of $Q = 0\cdot618$ (1) Å, $\theta = 88\cdot8$ (2)°, $\varphi = 104\cdot3$ (1)° for the Cr complex and $Q = 0\cdot623$ (2) Å, $\theta = 86\cdot8$ (2)°, $\varphi = 107\cdot6$ (2)° for the Co complex (Cremer & Pople, 1975). The ring-puckering amplitude is measured by Q, the chair to boat transition is defined by θ (0° or 180° = chair, 90° = boat), and the boat to twist-boat interconversion is given by the pseudorotation angle φ (0° = boat, 30° = twist-boat, 60° = boat, 90° = twist-boat,···).

In contrast to the chromium tetraammine complex, the chelate ring of the tetraaqua(pyrophosphato)-chromium(III) trihydrate complex (Merritt, Sundaralingam & Dunaway-Mariano, 1981) is in a boat conformation [$Q = 0\cdot575$ (3) Å, $\theta = 96\cdot2$ (4)°, $\varphi = 306\cdot7$ (3)°]. The Cr—H_2O coordination bonds are 0·1 Å shorter [average of 1·97 (2) Å] than the Co—NH_3 distances. The Cr to phosphate ligand oxygen distances, 1·966 (3) and 1·935 (3) Å, are significantly different in the chromium tetraaqua complex while these distances are nearly identical in the chromium tetraammine complex (Fig. 2).

The two water molecules of hydration both engage in four hydrogen-bonding interactions. Except for the one hydrogen bond between the two water molecules, the ammonia ligands serve as hydrogen-bond donors while the available phosphate O atoms serve as hydrogen-bond acceptors. A list of hydrogen bonds is given in Table 2. The hydrogen-bonding networks for the isomorphous Cr and Co complexes are nearly identical. The largest difference is 0·28 Å for the N(2)···O(*W*2) hydrogen bond. The Cr tetraammine complex has two intramolecular hydrogen bonds between the ammonia ligands and the pyrophosphate moiety [N(3)—H3(N3)···O2(P2) and N(4)—H2(N4)···O3(P1)], while the tetraaquachromium complex does not exhibit any intramolecular hydrogen bonding.

Yeast inorganic pyrophosphatase cleaves $Cr(NH_3)_4HP_2O_7$ with a maximum velocity twice as fast as observed for $Co(NH_3)_4HP_2O_7$ (Knight *et al.*, 1983). This may be partially due to the Cr—NH_3 coordination bonds which are more nearly equal to the Mg—H_2O coordination distances (Calvo, 1967) than are the shorter Cr—NH_3 bonds. In contrast, yeast inorganic pyrophosphatase hydrolyzes $Cr(H_2O)_4$PP with a maximal velocity 20 times that of $Cr(NH_3)_4$PP (Knight *et al.*, 1983). Fig. 3 shows an overlay of the chromium tetraammine and chromium tetraaqua pyrophosphate complexes. The two structures differ principally with respect to the chelate-ring pucker. The conformation of the chromium tetraaqua complex is stabilized by intermolecular hydrogen bonds to symmetry-related molecules and water of hydration (Merritt, Sundaralingam & Dunaway-Mariano, 1981) while the chromium tetraammine complex is primarily stabilized by intramolecular hydrogen bonds between the ammonia ligands and phosphate O atoms. It is interesting that this is the reverse of the situation observed in solution where the ring conformers of β,γ-bidentate $Cr(H_2O)_4$ATP are believed to be stabilized by intramolecular hydrogen bonds between water ligands and phosphate O atoms (Dunaway-Mariano & Cle-

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38934 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

land, 1980) while the ring conformers of the tetraammine complex are apparently not intramolecularly hydrogen bonded. The results from pyrophosphatase and kinase binding studies suggest that the nature of the ligands (water *versus* ammonia in this case) probably plays a key role in enzyme catalysis.

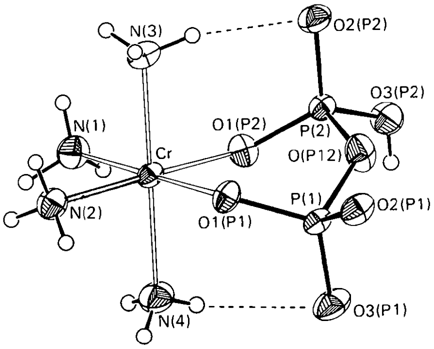

Fig. 1. An *ORTEP* drawing of the title compound showing nonhydrogen atoms as 50% thermal-probability ellipsoids and H atoms as spheres of arbitrary size.

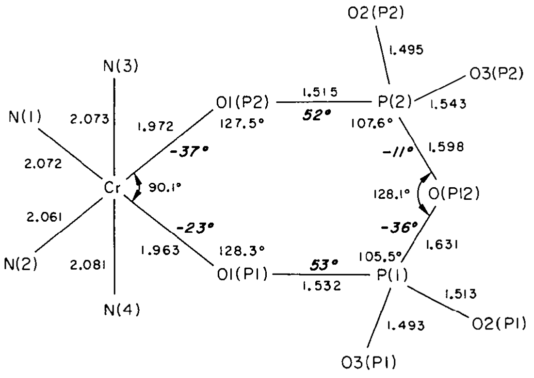

Fig. 2. Nonhydrogen bond distances (Å) for the title compound. Ring bond angles (°) and torsion angles (°) are also shown with the latter given in italics. The estimated standard deviations are 0·002 Å for bond lengths and 0·1° for bond angles and torsion angles.

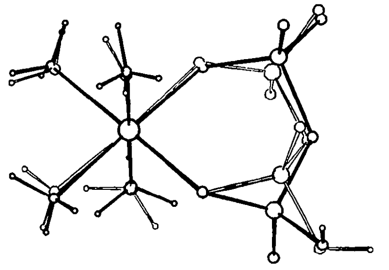

Fig. 3. An overlay diagram showing the tetraammine chromium complex (solid bonds) superimposed over the tetraaqua chromium complex (open bonds).

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Table 1. *Fractional positional parameters for all atoms of bidentate tetraammine(pyrophosphato)chromium(III) dihydrate*

Values are $\times 10^5$ for non-hydrogen atoms and $\times 10^3$ for H atoms.

$$B_{eq} = \tfrac{4}{3}\sum_i \sum_j \beta_{ij}\, \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq} or B(Å^2)
Cr	11423 (4)	45568 (2)	22040 (2)	1·40 (1)
P(1)	−15811 (6)	31011 (3)	9634 (4)	1·53 (1)
P(2)	−27046 (6)	41181 (3)	29946 (4)	1·53 (1)
O1(P1)	−2050 (18)	39169 (9)	9119 (10)	1·90 (2)
O2(P1)	−26299 (20)	30264 (10)	−1933 (11)	2·18 (3)
O3(P1)	−8195 (23)	21717 (10)	14253 (13)	2·76 (3)
O(P12)	−30450 (19)	34782 (11)	18514 (12)	2·59 (3)
O1(P2)	−7027 (18)	41717 (10)	32617 (11)	1·97 (2)
O2(P2)	−36395 (20)	50637 (10)	27986 (13)	2·43 (3)
O3(P2)	−36345 (19)	35638 (10)	39491 (11)	2·33 (3)
N(1)	25176 (24)	52081 (13)	36034 (15)	2·35 (3)
N(2)	31464 (22)	49292 (12)	11398 (14)	2·11 (3)
N(3)	−1877 (23)	58234 (11)	17335 (13)	2·02 (3)
N(4)	24927 (24)	32767 (12)	26131 (16)	2·59 (4)
O(*W*1)	23199 (27)	35684 (15)	55313 (17)	4·22 (4)
O(*W*2)	36023 (27)	32014 (14)	−2977 (19)	4·19 (4)
H(O3P2)	−316 (5)	309 (3)	420 (3)	5·6 (9)
H1(N1)	224 (6)	482 (3)	415 (3)	5·8 (9)
H2(N1)	216 (4)	577 (2)	369 (2)	2·6 (5)
H3(N1)	375 (5)	521 (2)	357 (3)	4·2 (7)
H1(N2)	416 (5)	501 (2)	159 (3)	4·7 (8)
H2(N2)	327 (4)	447 (2)	65 (3)	3·3 (6)
H3(N2)	293 (4)	547 (2)	75 (3)	3·1 (6)
H1(N3)	−16 (4)	594 (2)	102 (3)	3·9 (7)
H2(N3)	28 (5)	630 (2)	208 (2)	3·9 (7)
H3(N3)	−131 (5)	571 (3)	182 (3)	4·5 (8)
H1(N4)	315 (8)	337 (4)	309 (5)	11·1 (18)
H2(N4)	188 (6)	294 (3)	286 (4)	8·2 (13)
H3(N4)	309 (8)	299 (4)	207 (5)	11·7 (18)
H1(*W*1)	275 (6)	387 (3)	611 (3)	6·8 (11)
H2(*W*1)	135 (5)	346 (3)	570 (3)	5·5 (9)
H1(*W*2)	478 (6)	316 (3)	−40 (4)	6·9 (11)
H2(*W*2)	333 (5)	268 (3)	1 (3)	4·9 (8)

Table 2. *List of hydrogen bonds for the title compound*

		Translation			Distances			Angle
A—H···*B*	Code*	*x*	*y*	*z*	*A*—H	H···*B*	*A*···*B*	*A*—H···*B*
O3(P2)—H(O3P2)···O2(P1)	2	0	0	0	0·79 Å	1·73 Å	2·511 Å	167°
N(1)—H1(N1)—O(*W*1)	1	0	0	0	0·86	2·35	3·189	163
N(1)—H2(N1)—O3(P1)	4	0	0	0	0·83	2·19	3·000	167
N(1)—H3(N1)—O2(P2)	1	1	0	0	0·93	2·21	3·084	158
N(2)—H1(N2)—O2(P2)	1	1	0	0	0·90	2·10	2·993	172
N(2)—H2(N2)—O(*W*2)	1	0	0	0	0·86	2·09	2·943	170
N(2)—N3(N2)—O2(P1)	3	0	1	0	0·88	2·19	3·050	166
N(3)—H1(N3)—O1(P1)	3	0	1	0	0·84	2·27	3·109	172
N(3)—H2(N3)—O3(P1)	4	0	0	0	0·84	2·13	2·896	153
N(3)—H3(N3)—O2(P2)	1	0	0	0	0·87	2·32	3·112	153
N(4)—H1(N4)—O3(P2)	1	1	0	0	0·73	2·56	3·229	153
N(4)—H2(N4)—O3(P1)	1	0	0	0	0·72	2·75	3·158	118
N(4)—H2(N4)—O(*W*2)	3	0	0	0	0·72	2·89	3·235	112
O(*W*1)—H1(*W*1)—O2(P2)	3	0	1	1	0·84	2·03	2·839	163
O(*W*1)—H2(*W*1)—O3(P1)	2	0	0	0	0·78	2·07	2·817	162
O(*W*2)—H1(*W*2)—O2(P1)	1	1	0	0	0·90	1·95	2·828	165
O(*W*2)—H2(*W*2)—O(*W*1)	2	0	0	−1	0·84	1·99	2·819	170

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

References

CALVO, C. (1967). *Acta Cryst.* **23**, 289–295.

CORNELIUS, R. D., HART, P. A. & CLELAND, W. W. (1977). *Inorg. Chem.* **16**, 2799–2805.

CREMER, D. & POPLE, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.

CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–109.

DUNAWAY-MARIANO, D. & CLELAND, W. W. (1980). *Biochemistry*, **19**, 1506–1515.

HAROMY, T. P. (1982). *Crystallographic Studies of Metal–Polyphosphate Chelate Complexes and the Investigation of the Substrate Conformational Requirements and Mechanisms of Polyphosphate Processing Enzymes*. PhD Thesis, pp. 24–27. Univ. of Wisconsin–Madison.

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 148–151. Birmingham: Kynoch Press.

JOHNSON, C. K. (1976). *ORTEP*-II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.

KNIGHT, W. B., TING, S.-J., CHUANG, S., DUNAWAY-MARIANO, D., HAROMY, T. P. & SUNDARALINGAM, M. (1983). *Arch. Biochem. Biophys.* **227**, 302–309.

MERRITT, E. A. & SUNDARALINGAM, M. (1980). *Acta Cryst.* B**36**, 2576–2584.

MERRITT, E. A., SUNDARALINGAM, M. & DUNAWAY-MARIANO, D. (1981). *J. Am. Chem. Soc.* **103**, 3565–3567.

PFEIFFER, P. (1905). *Chem. Ber.* **38**, 3592–3601.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

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Aluminate Sodalite $Ca_8[Al_{12}O_{24}](WO_4)_2$* at Room Temperature

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Abstract. $M_r = 1524\cdot1$, orthorhombic, $Aba2$, $a = 26\cdot151\ (2)$, $b = 13\cdot075\ (1)$, $c = 9\cdot319\ (1)$ Å, $V = 3186\cdot3\ (8)$ Å^3, $Z = 4$, $D_x = 3\cdot177$ Mg m^{-3}, $F(000) = 2880$, $\lambda(\text{Mo } K\alpha) = 0\cdot71069$ Å, $\mu(\text{Mo } K\alpha) = 2\cdot638$ mm^{-1}, twinned crystal, $R = 0\cdot041$ for 2671 independent reflections including 816 detwinned superimposed reflections. The sodalite framework is entirely composed of AlO_4 tetrahedra and its partial collapse is anisotropic in contrast to most of the other usually cubic sodalites. The anisotropy can be attributed to interactions between framework oxygens and the WO_4 group which is rotated by ~45° about the [001] direction out of the position where its threefold axes match those of the framework. Two reversible phase transitions occur at 614 and 656 K.

Introduction. The common feature of all members of the sodalite family is a framework of corner-linked TO_4 tetrahedra ($T = Si^{4+}, Al^{3+}, B^{3+}, Ga^{3+}, Ge^{4+}, Be^{2+}, \ldots$). It is convenient to subdivide the family according to the T cations; *e.g.* the naturally occurring aluminosilicate sodalites have a framework composition $[Al_6Si_6O_{24}]^{6-}$ and aluminate sodalites are characterized by $[Al_{12}O_{24}]^{12-}$ frameworks. The T cations occupy the vertices of truncated octahedra which are connected to each other *via* their 4-rings and 6-rings in such a way that the available space is completely filled. The truncated octahedra are often referred to as sodalite cages or, especially in zeolite chemistry, as β-cages. They accommodate the cage cations and cage anions, both of which exhibit a great variety as to the occurring chemical species. The diversity is limited mainly by the sizes of the cage ions and by the demands on charge compensation for the negatively charged framework.

The framework adapts itself to the sizes and, as will be shown in this and subsequent works, also to the shapes of the cage ions and it is this adaptation which is referred to as 'folding', 'partial collapse' or 'crumpling' of the sodalite framework. The folding is accomplished by cooperative rotations of the TO_4 tetrahedra (see, *e.g.*, Fig. 1 of Taylor, 1972). For ideal, cubic sodalites, the tetrahedra rotate about the $\bar{4}$ axes and the amount of the rotation is measured by the so-called tilt angle φ. This angle has the same absolute value for all tetrahedra and, therefore, one can call this behaviour isotropic folding. The symmetry of the ideal framework is thereby reduced from $Im3m$ to $I\bar{4}3m$ (ordering on the T sites would further reduce the symmetry, as is the case for most of the aluminosilicate sodalites). Hence, $I\bar{4}3m$ is the highest possible symmetry of a partially collapsed sodalite. Well-established geometrical relationships exist between the tilt angle and the lattice parameters, the tetrahedra edge lengths and the fractional coordinates of the framework oxygens (Taylor, 1972; Nyman & Hyde, 1981; Koch & Hellner, 1981). For non-ideal, perhaps non-cubic, sodalites the situation is more complicated since there is no longer one single tilt angle for the whole framework, but individual tetrahedra have to be considered. New concepts for a description of the folding in those cases had, therefore, to be developed. This has been done for the group of aluminate sodalites, for which the term 'anisotropic folding' has been used (Depmeier, 1983). A method to describe the anisotropic folding quantitatively will be published elsewhere (Depmeier, to be published).

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* Hexaaluminium tetracalcium dodecaoxide tungstate.

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