

## Structure of $\alpha,\gamma$ -Bidentate Tetraammine(dihydrogentriphosphato)cobalt(III) Monohydrate

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**Abstract.**  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{P}_3\text{O}_{10})]\cdot\text{H}_2\text{O}$ , monoclinic,  $P2_1/n$ ,  $a = 7.234(1)$ ,  $b = 14.106(1)$ ,  $c = 12.113(1)$  Å,  $\beta = 92.909(5)^\circ$ ,  $V = 1234.5(4)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 2.152$  Mg m<sup>-3</sup>;  $R = 0.046$  for 2369 independent reflections with  $F_o > 3\sigma(F_o)$ . This coordination isomer contains an eight-membered chelate ring in a boat conformation stabilized by two interligand hydrogen bonds from the axial amines above and below the chelate ring to the  $\beta$  and  $\gamma$  phosphates. The O(1)–Co–O(10) dentation angle of  $94.6(2)^\circ$  and O(1)···O(10) bite of  $2.831(4)$  Å are essentially the same as in the previously reported  $\beta,\gamma$ -bidentate isomer of the compound which contains a six-membered chelate ring.

**Introduction.** The coordination geometries of polyphosphate chains complexed with substitution-inert metal ions serve as models for the metal–phosphate moieties of biologically important complexes. We have previously reported the chirality, conformation, and biological relevance of the  $\beta,\gamma$ -bidentate coordination isomer of  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{P}_3\text{O}_{10})]\cdot\text{H}_2\text{O}$  (Merritt, Sundaralingam, Cornelius & Cleland, 1978; Merritt & Sundaralingam, 1980), which is a fragment of the enzymatically active substrate  $\beta,\gamma$ -bidentate  $[\text{Co}(\text{NH}_3)_4\text{ATP}]$ . We have also reported the structure of an  $\alpha,\beta,\gamma$ -tridentate complex  $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{P}_3\text{O}_{10})]$  (Merritt & Sundaralingam, 1977). The  $\beta,\gamma$ -bidentate complex contains a six-membered chelate ring. The present isomeric  $\alpha,\gamma$ -bidentate complex contains an eight-membered chelate ring instead, and is formed in small amounts in the same reaction solution used to prepare the  $\beta,\gamma$ -bidentate complex (Cornelius, Hart & Cleland, 1977). A communication on the initial characterization of the  $\alpha,\gamma$ -bidentate complex by <sup>31</sup>P NMR and X-ray crystallography has been presented elsewhere (Merritt, Sundaralingam & Cornelius, 1980). Although no enzymes are currently known to use metal–nucleotide substrates with  $\alpha,\gamma$ -bidentate coordination, it is interesting to compare the structural details of such alternate coordination modes.

The crystal data are given in the *Abstract*. The equivalent  $P2_1/c$  setting has  $c = 13.790(1)$  Å and  $\beta = 118.686(5)^\circ$ . Intensity data for a crystal measuring  $0.05 \times 0.10 \times 0.20$  mm were collected using Ni-filtered Cu radiation on an Enraf–Nonius CAD-4 diffractometer. 2608 unique reflections were measured using a  $\theta$ – $2\theta$  scan in bisecting geometry. A correction for crystal decay based on three standard reflections measured after every two hours of X-ray exposure, an empirical absorption correction based on the Eulerian angle  $\varphi$ , and a Lorentz–polarization correction were all applied during data reduction.

The direct-methods program *MULTAN* (Main, Woolfson, Lessinger, Germain & Declercq, 1974) produced a unique phase assignment for the 437 reflections with largest  $E$  values based on a set of three origin-defining reflections (375, 3, 8, 12, 22i) and a phase of  $360^\circ$  for the 0,16,0 reflection from  $\sum_1$  relationships. The 19 non-hydrogen atoms of the structure appeared among the top 21 peaks of the  $E$  map. These 19 atoms were refined by block-diagonal least squares with anisotropic thermal parameters to an agreement index  $R = 0.060$ . At this point the 16 H atoms were found from a difference Fourier synthesis. Full-matrix least-squares refinement including positional and isotropic thermal parameters for the H atoms yielded a final value of  $R = 0.046$ . Maximum shift/error for a non-hydrogen parameter during the final cycle of refinement was 0.27. The 2369 reflections for which  $F_o > 3\sigma(F_o)$  were given weight  $w = [\sigma(F_o)^2 + (0.03F_o)^2]^{-1}$ . The  $R$  values given above include only these reflections. The final  $R$  value including the 239 zero-weighted reflections with  $F_o < 3\sigma(F_o)$  was 0.052. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974).\*

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35730 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

**Discussion.** Fractional atomic coordinates for the  $\alpha,\gamma$ -bidentate  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{P}_3\text{O}_{10})]\cdot\text{H}_2\text{O}$  complex (Fig. 1) are given in Table 1. Bond distances, bond angles and torsion angles are given in Fig. 2 and Table 2. Hydrogen-bonding parameters are given in Table 3.

The principal feature of interest in this compound is the eight-membered chelate ring formed by the  $\alpha,\gamma$  coordination of the triphosphate chain to the Co atom. The ring is in a boat conformation (Figs. 1 and 3), with atoms P(1)—O(4)—P(2)—O(7) essentially coplanar. The Cremer & Pople (1975) parameters describing the Co—O(1)—P(1)—O(4)—P(2)—O(7)—P(3)—O(10) ring conformation are  $Q_2 = 1.423$  (2) Å,  $\varphi_2 = 38.9$  (1)°,  $Q_3 = 0.122$  (3) Å,  $\varphi_3 = 246$  (1)°, and  $Q_4 = 0.124$  (4) Å. The observed conformation is additionally stabilized by the two interligand hydrogen bonds from the axial amines to  $\beta$  and  $\gamma$  phosphate oxygens: N(2)···O(6) = 3.008 (4) and N(4)···O(8) = 3.289 (4) Å. The Co—N distances for these two ammine groups are

Table 1. Positional and isotropic thermal parameters for  $\alpha,\gamma$ -bidentate  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{P}_3\text{O}_{10})]\cdot\text{H}_2\text{O}$

For non-hydrogen atoms  $B_{\text{eq}} = \frac{4}{3} \sum_i \sum_j \beta_{ij} (\mathbf{a}_i \cdot \mathbf{a}_j)$ .

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{eq}}/B$ (Å <sup>2</sup> )
Co	0.25637 (8)	0.60117 (3)	0.78525 (4)	1.40
P(1)	0.3821 (1)	0.6734 (1)	1.0382 (1)	1.66
P(2)	0.1561 (1)	0.8397 (1)	0.9748 (1)	1.77
P(3)	−0.1036 (1)	0.7052 (1)	0.8716 (1)	1.56
O(1)	0.3197 (4)	0.6146 (2)	0.9414 (2)	2.60
O(2)	0.2619 (4)	0.6458 (2)	1.1346 (2)	2.57
O(3)	0.5848 (4)	0.6690 (2)	1.0695 (2)	2.66
O(4)	0.3416 (4)	0.7823 (2)	1.0123 (2)	2.59
O(5)	0.1133 (5)	0.9048 (2)	1.0661 (3)	3.31
O(6)	0.1784 (4)	0.8764 (2)	0.8618 (2)	2.80
O(7)	0.0011 (4)	0.7579 (2)	0.9740 (2)	2.13
O(8)	−0.1933 (4)	0.6197 (2)	0.9287 (2)	2.42
O(9)	−0.2456 (4)	0.7727 (2)	0.8223 (2)	2.34
O(10)	0.0293 (3)	0.6713 (2)	0.7902 (2)	2.08
N(1)	0.1926 (5)	0.5827 (2)	0.6309 (3)	2.27
N(2)	0.3765 (4)	0.7201 (2)	0.7471 (3)	2.15
N(3)	0.4819 (4)	0.5309 (2)	0.7712 (3)	2.30
N(4)	0.1264 (5)	0.4858 (2)	0.8242 (3)	2.56
O(W)	0.1291 (5)	0.5457 (2)	0.3753 (3)	3.88
H(1A)	0.117 (6)	0.630 (3)	0.608 (4)	2.6 (10)
H(1B)	0.104 (8)	0.525 (4)	0.617 (5)	5.3 (15)
H(1C)	0.277 (12)	0.574 (6)	0.607 (7)	11.6 (24)
H(2A)	0.382 (7)	0.739 (4)	0.678 (5)	5.0 (14)
H(2B)	0.482 (6)	0.740 (3)	0.776 (3)	2.2 (9)
H(2C)	0.297 (8)	0.769 (4)	0.760 (5)	5.8 (15)
H(3A)	0.540 (7)	0.532 (4)	0.826 (5)	5.2 (14)
H(3B)	0.558 (7)	0.552 (4)	0.726 (5)	4.5 (13)
H(3C)	0.439 (7)	0.475 (4)	0.745 (5)	4.2 (12)
H(4A)	0.210 (9)	0.436 (5)	0.829 (6)	7.6 (18)
H(4B)	0.069 (13)	0.469 (6)	0.796 (9)	14.2 (30)
H(4C)	0.075 (8)	0.500 (4)	0.885 (5)	6.0 (16)
H(W1)	0.209 (6)	0.512 (3)	0.388 (4)	2.6 (10)
H(W2)	0.191 (9)	0.597 (4)	0.345 (5)	6.6 (16)
H(O2)	0.288 (9)	0.685 (5)	1.205 (5)	6.0 (16)
H(O8)	−0.250 (7)	0.646 (3)	0.974 (4)	3.2 (12)

Table 2. Some bond and torsion angles (°) in  $\alpha,\gamma$ -bidentate  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{P}_3\text{O}_{10})]\cdot\text{H}_2\text{O}$

The mean estimated standard deviations in bond and torsion angles are 0.2 and 0.3° respectively.

N(1)—Co—N(2)	88.5	O(1)—P(1)—O(2)	107.2
N(1)—Co—N(3)	90.4	O(1)—P(1)—O(3)	115.5
N(1)—Co—N(4)	91.6	O(1)—P(1)—O(4)	109.7
N(1)—Co—O(1)	177.8	O(2)—P(1)—O(3)	112.4
N(1)—Co—O(10)	86.4	O(2)—P(1)—O(4)	106.7
N(2)—Co—N(3)	91.8	O(3)—P(1)—O(4)	105.0
N(2)—Co—N(4)	177.4		
N(2)—Co—O(1)	93.5	O(4)—P(2)—O(5)	107.7
N(2)—Co—O(10)	87.5	O(4)—P(2)—O(6)	107.9
N(3)—Co—N(4)	90.7	O(4)—P(2)—O(7)	102.2
N(3)—Co—O(1)	88.7	O(5)—P(2)—O(6)	120.7
N(3)—Co—O(10)	176.7	O(5)—P(2)—O(7)	106.1
N(4)—Co—O(1)	86.5	O(6)—P(2)—O(7)	110.7
N(4)—Co—O(10)	89.9		
O(1)—Co—O(10)	94.6	O(7)—P(3)—O(8)	102.0
		O(7)—P(3)—O(9)	107.5
Co—O(1)—P(1)—O(4)	22.0	O(7)—P(3)—O(10)	111.4
O(1)—P(1)—O(4)—P(2)	55.8	O(8)—P(3)—O(9)	112.2
P(1)—O(4)—P(2)—O(7)	2.9	O(8)—P(3)—O(10)	110.2
O(4)—P(2)—O(7)—P(3)	−105.7	O(9)—P(3)—O(10)	113.1
P(2)—O(7)—P(3)—O(10)	48.7		
O(7)—P(3)—O(10)—Co	49.4		
P(3)—O(10)—Co—O(1)	−17.1		
O(10)—Co—O(1)—P(1)	−71.3		

Table 3. Hydrogen bonding in  $\alpha,\gamma$ -bidentate  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{P}_3\text{O}_{10})]\cdot\text{H}_2\text{O}$

Donor—H...Acceptor	Symmetry code*	<i>D</i> ... <i>A</i>	<i>H</i> ... <i>A</i>	$\angle D-H...A$
N(1)—H(1B)...O(W)	[3, 0 1 1]	2.947 Å	1.97 Å	155°
N(1)—H(1C)...O(5)	[2, 0 1 −1]	3.186	2.53	158
N(2)—H(2B)...O(9)	[1, 1 0 0]	2.933	2.07	169
N(2)—H(2C)...O(6)	[1, 0 0 0]	3.008	2.16	154
N(3)—H(3A)...O(8)	[1, 1 0 0]	3.205	2.56	143
N(3)—H(3B)...O(5)	[2, 0 1 −1]	2.853	2.09	149
N(3)—H(3C)...O(6)	[4, 0 −1 1]	2.916	2.05	160
N(4)—H(4A)...O(3)	[3, 1 1 2]	3.243	2.39	153
N(4)—H(4B)...O(W)	[3, 0 1 1]	3.000	2.47	155
N(4)—H(4C)...O(8)	[1, 0 0 0]	3.289	2.65	132
O(W)—H(WA)...O(5)	[4, 0 −1 1]	2.791	2.04	169
O(W)—H(WB)...O(9)	[2, 0 1 −1]	2.803	1.92	157
O(2)—H(O2)...O(9)	[2, 0 1 0]	2.551	1.57	158
O(8)—H(O8)...O(3)	[1, −1 0 0]	2.499	1.74	161
Mean e.s.d.		0.004	0.06	6

\* The acceptor-atom symmetry code is given as the *x*, *y* and *z* translation preceded by the symmetry operation, as follows: (1) *x*, *y*, *z*; (2) 0.5 + *x*, −*y*, 0.5 + *z*; (3) −*x*, −*y*, −*z*; (4) 0.5 − *x*, *y*, 0.5 − *z*.

significantly longer than those for N(1) and N(3), which lie in the same plane as the ligated oxygens.

The four non-ring O atoms from the  $\alpha$  and  $\gamma$  phosphates are involved in strong hydrogen-bonding interactions with neighboring molecules: O(2)···O(9) = 2.551 (4) and O(8)···O(3) = 2.499 (4) Å. These are the only two direct interactions between phosphate groups; all others are mediated by ammine or water molecules. Similar short phosphate–phosphate interac-

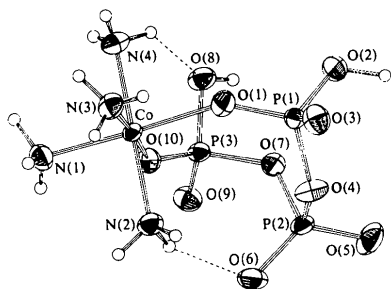


Fig. 1. An ORTEP (Johnson, 1965) plot of the  $\alpha,\gamma$ -bidentate  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{P}_2\text{O}_{10})]$  complex with thermal ellipsoids drawn at the 50% probability level. The eight-membered chelate-ring conformation is stabilized by two interligand hydrogen bonds, one above and the other below the ring.

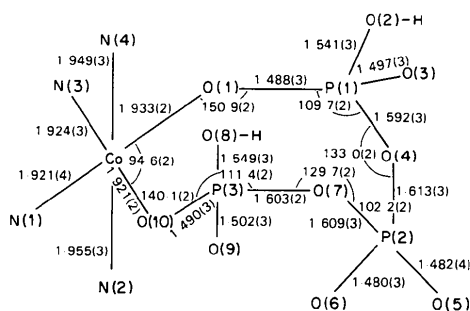


Fig. 2. Bond distances (Å) and bond angles ( $^\circ$ ) for  $\alpha,\gamma$ -bidentate  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{P}_2\text{O}_{10})]$ . Additional bond angles about the Co and P atoms are given in Table 2, as are the chelate-ring torsion angles.

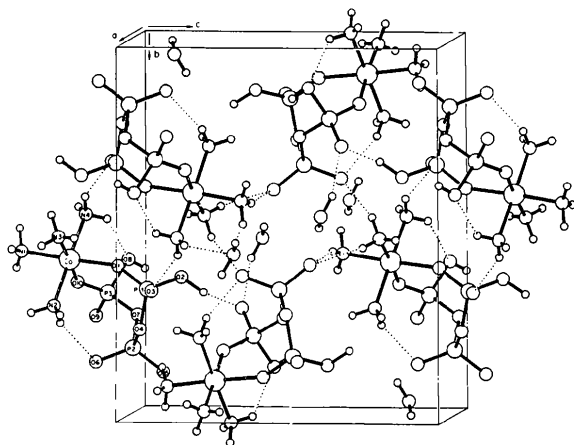


Fig. 3. Packing diagram of  $\alpha,\gamma$ -bidentate  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{P}_2\text{O}_{10})] \cdot \text{H}_2\text{O}$ , with hydrogen bonds shown as dotted lines.

tions are also seen in the previously reported polyphosphato-cobaltamine complexes (Merritt & Sundaralingam, 1980). The two ammine hydrogens H(1A) and H(2A) do not appear to be involved in hydrogen bonding.

The conformation of this eight-membered ring complex may be compared with that of the  $\beta,\gamma$ -bidentate isomer containing a six-membered ring. The dentation angle in the two isomers is essentially the

same [ $94.6(2)$  vs  $93.7(2)^\circ$ ], as is the bite [ $\text{O}(1)\cdots\text{O}(10) = 2.831(4)$  vs  $\text{O}(5)\cdots\text{O}(10) = 2.818(8)$  Å in the  $\beta,\gamma$  isomer]. The conformation of the fragment  $\text{O}(1)\text{—Co—O}(10)\text{—P}(3)\text{—O}(7)$  in the eight-membered ring is very close to that of the fragment  $\text{O}(5)\text{—Co—O}(10)\text{—P}(3)\text{—O}(7)$  in the six-membered ring; the torsion angles about the bonds bridging the central atom O(10) in the two complexes are  $-17.1(3)$  and  $49.4(3)^\circ$  vs  $-18.2(6)$  and  $45.4(6)^\circ$  respectively. In both rings this allows a potential hydrogen bond from the axial ammine to O(8), albeit a rather long one in the  $\alpha,\gamma$  isomer [ $3.289(4)$  vs  $3.003(10)$  Å]. The similarity in the dentation values is possible because of the flexibility of the phosphate chain. In the  $\alpha,\gamma$  complex the phosphate chain doubles back on itself, yielding a P—P angle of  $86.0(1)^\circ$  as opposed to  $116.1(1)^\circ$  in the  $\beta,\gamma$  complex. The bridging Co—O—P angles in the  $\alpha,\gamma$  complex have widened to  $140.1(2)$  and  $150.9(2)^\circ$  from the  $\beta,\gamma$ -complex values of  $128.9(4)$  and  $129.8(3)^\circ$ . In both complexes the  $\beta$ -phosphate diester O—P—O angle is near  $102^\circ$ , which is typical of phosphodiester bond angles.

The disparity in P—O bond lengths in the  $\alpha,\gamma$  complex about the bridging oxygen atom O(4),  $0.021$  Å =  $7\sigma$ , is typical of polyphosphate chains (Merritt & Sundaralingam, 1980); the P—O bond lengths about the other bridging oxygen O(7) are atypically symmetric. The P—O bond lengths involving the chelated oxygens O(1) and O(10) are in the same range as those of the exocyclic anionic P—O bonds.

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