Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

Pyridinium diaquabis(methylenediphosphonato-κ^2O,O')chromate(III) tetrahydrate

Kina Van der Merwe,* Hendrik G. Visser and J. A. Venter

Department of Chemistry, University of the Free State, PO Box 339, Bloemfontein 9330, South Africa
Correspondence e-mail: kinavdmerwe@gmail.com

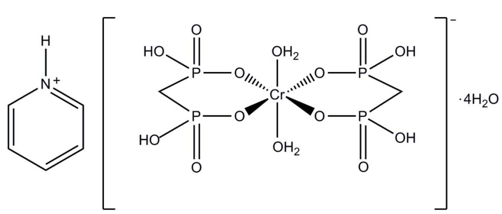
Received 14 July 2010; accepted 20 July 2010

Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.013 Å; disorder in solvent or counterion; R factor = 0.024; wR factor = 0.070; data-to-parameter ratio = 14.7.

In the title complex, $(C_5H_6N)[Cr(CH_4O_6P_2)_2(H_2O)_2]\cdot 4H_2O$, the Cr^{III} atom, lying on an inversion centre, is coordinated by two bidentate methylene diphosphonate ligands and two water molecules in a distorted octahedral coordination geometry. The pyridinium cation is located on an inversion centre, with an N atom and a C atom sharing a position each at a half occupancy. A three-dimensional network is constructed by O—H···O, N—H···O and C—H···O hydrogen bonds between the pyridinium cation, complex anion and uncoordinated water molecules.

Related literature

For general background to metal-organic frameworks with diphosphonic acids, see: Barthelet *et al.* (2002). For related structures, see: Byun *et al.* (2006); Suh *et al.* (1997); Van der Merwe *et al.* (2009); Visser *et al.* (2010).



Experimental

Crystal data

$(C_5H_6N)[Cr(CH_4O_6P_2)_2(H_2O)_2]\cdot$-$4H_2O$
M_r = 588.17
Triclinic, $P\bar{1}$
a = 7.206 (5) Å
b = 7.485 (5) Å
c = 10.984 (5) Å
α = 107.085 (5)°
β = 106.128 (5)°
γ = 94.496 (5)°
V = 535.7 (6) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 0.92 mm^{-1}
T = 100 K
0.22 × 0.16 × 0.08 mm

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; (Bruker, 2001) T_{min} = 0.843, T_{max} = 0.931
8784 measured reflections
2632 independent reflections
2483 reflections with $I > 2\sigma(I)$
R_{int} = 0.020

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.024
$wR(F^2)$ = 0.070
S = 1.05
2632 reflections
179 parameters
16 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.47 e Å^{-3}
$\Delta\rho_{min}$ = −0.62 e Å^{-3}

Table 1
Selected bond lengths (Å).

Cr1—O1	1.991 (4)	Cr1—O7	1.964 (4)
Cr1—O2	1.956 (4)		

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C1—H4···O6^{i}	0.97	2.49	3.346 (7)	147
C4—H4A···O9^{ii}	0.93	2.16	2.93 (7)	140
N1—H1···O9^{ii}	0.86	2.32	3.03 (5)	141
O1—H1A···O6^{i}	0.80 (6)	1.83 (6)	2.634 (6)	176 (9)
O1—H1B···O4^{iii}	0.83 (6)	1.87 (6)	2.704 (6)	177 (9)
O3—H3···O8^{iv}	0.82	1.83	2.629 (6)	163
O5—H6···O4^{ii}	0.83 (5)	1.80 (5)	2.619 (6)	175 (10)
O8—H7···O6^{v}	0.83 (6)	1.86 (6)	2.687 (6)	171 (9)
O8—H8···O9	0.85 (7)	1.94 (8)	2.748 (7)	158 (11)
O9—H9A···O4	0.83 (6)	2.00 (6)	2.833 (6)	179 (10)
O9—H10···O8^{vi}	0.84 (7)	1.99 (7)	2.820 (7)	174 (13)

Symmetry codes: (i) $-x+1, -y+2, -z+1$; (ii) $-x, -y+1, -z+1$; (iii) $x+1, y, z$; (iv) $-x+1, -y+2, -z+2$; (v) $x, y, z+1$; (vi) $-x, -y+2, -z+2$.

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT-Plus* (Bruker, 2007); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXTL*.

The University of the Free State and Professor A. Roodt are gratefully acknowledged for financial support.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HY2333).

References

Barthelet, K., Riou, D. & Férey, G. (2002). *Acta Cryst.* C**58**, m264–m265.
Brandenburg, K. (1999). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
Bruker (2001). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2007). *APEX2* and *SAINT-Plus*. Bruker AXS Inc., Madison, Wisconsin, USA.
Byun, J. C., Yoon, C. H., Mun, D. H., Kim, K. J. & Park, Y. C. (2006). *Bull. Korean Chem. Soc.* **27**, 687–693.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Suh, J.-S., Park, S.-J., Lee, K.-W., Suh, I.-H., Lee, J.-H., Song, J.-H. & Oh, M.-R. (1997). *Acta Cryst.* C**53**, 432–434.
Van der Merwe, K. A., Visser, H. G. & Venter, J. A. (2009). *Acta Cryst.* E**65**, m1394.
Visser, H. G., Venter, J. A. & Van der Merwe, K. A. (2010). *Acta Cryst.* E**66**, m159.

supplementary materials

Acta Cryst. (2010). E**66**, m1011-m1012   [**doi:10.1107/S1600536810028990**]

Pyridinium diaquabis(methylenediphosphonato-κ^2O,O')chromate(III) tetrahydrate

K. Van der Merwe, H. G. Visser and J. A. Venter

Comment

The title compound forms part of an ongoing study in our group involving methylene diphosphonate and its coordination to various metal cores. (Van der Merwe *et al.*, 2009; Visser *et al.*, 2010). Diphosphonic acids are useful for the synthesis of metal-organic frameworks exhibiting microporous properties (Barthelet *et al.*, 2002).

The Cr^{III} ion in the title complex is in a distorted octahedral environment (Fig. 1), with Cr—O bond distances ranging from 1.956 (4) to 1.991 (4) Å (Table 1). All the bond distances and angles are well within the normal range (Byun *et al.*, 2006; Suh *et al.*, 1997). The pyridinium cation is located on an inversion centre and an N atom and a C atom share a position at a half occupancy for each atom. A three-dimensional network is provided by numerous hydrogen bonds between the pyridinium cation, complex anion and uncoordinated water molecules (Table 2).

Experimental

$CrCl_3.6H_2O$ (0.092 g, 0.347 mmol) was dissolved in water (40 ml) and ammonium hydroxide was gradually added dropwise in order to precipitate Cr(III) hydroxide. Methylene diphosphonate (0.347 g, 2 mmol) was added to the $Cr(OH)_3$ and water (40 ml). The reaction solution was heated on an oil bath for 5 h at 100°C, after which pyridine (10 ml) was added to the solution. Boiling H_2O (30 ml) was added and the solution was centrifuged. Green crystals of the title compound crystallized from the filtrate after several days.

Refinement

C-bound H atoms were positioned geometrically and refined as riding atoms, with C—H = 0.97 Å and $U_{iso}(H) = 1.2U_{eq}(C)$. The H atoms attached to hydroxy groups and water molecules were located on a difference Fourier map and refined isotropically except H3, which was refined as riding, with O3—H3 = 0.82 Å and $U_{iso}(H3) = 1.5U_{eq}(O3)$. A 50% positional disorder was assigned to N1 and C4, which share a position of the pyridine ring, as this provided the best fit of the data. Short C—C bond interactions, probably due to this disorder, are observed for the pyridinium cation.

Figures

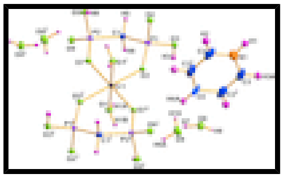


Fig. 1. Molecular structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (i) 1-x, 1-y, 1-z.]

Pyridinium diaquabis(methylenediphosphonato-κ^2*O*,*O*')chromate(III) tetrahydrate

Crystal data

$(C_5H_6N)[Cr(CH_4O_6P_2)_2(H_2O)_2]\cdot 4H_2O$	$Z = 1$
$M_r = 588.17$	$F(000) = 303$
Triclinic, $P\overline{1}$	$D_x = 1.823$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 7.206$ (5) Å	Cell parameters from 6300 reflections
$b = 7.485$ (5) Å	$\theta = 0.8–0.9°$
$c = 10.984$ (5) Å	$\mu = 0.92$ mm^{-1}
$\alpha = 107.085$ (5)°	$T = 100$ K
$\beta = 106.128$ (5)°	Cuboid, green
$\gamma = 94.496$ (5)°	0.22 × 0.16 × 0.08 mm
$V = 535.7$ (6) Å^3	

Data collection

Bruker APEXII CCD diffractometer	2483 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.020$
Absorption correction: multi-scan (*SADABS*; (Bruker, 2001)	$\theta_{max} = 28.3°$, $\theta_{min} = 4.1°$
$T_{min} = 0.843$, $T_{max} = 0.931$	$h = -9\rightarrow 9$
8784 measured reflections	$k = -9\rightarrow 6$
2632 independent reflections	$l = -14\rightarrow 14$

Refinement

Refinement on F^2	16 restraints
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.024$	$w = 1/[\sigma^2(F_o^2) + (0.0342P)^2 + 0.4874P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.070$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.05$	$\Delta\rho_{max} = 0.47$ e Å^{-3}
2632 reflections	$\Delta\rho_{min} = -0.62$ e Å^{-3}
179 parameters	

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	$U_{iso}*/U_{eq}$	Occ. (<1)
Cr1	0.5000	0.5000	0.5000	0.0082 (3)	
P2	0.2173 (2)	0.79359 (19)	0.41325 (14)	0.0086 (4)	
P1	0.29362 (19)	0.7622 (2)	0.69142 (14)	0.0085 (4)	
O2	0.4491 (6)	0.6457 (6)	0.6635 (4)	0.0110 (8)	

O5	−0.0069 (6)	0.7069 (6)	0.3539 (4)	0.0128 (8)	
O3	0.3700 (6)	0.8943 (6)	0.8418 (4)	0.0134 (8)	
H3	0.4774	0.9569	0.8570	0.020*	
O7	0.3373 (6)	0.6353 (6)	0.3947 (4)	0.0113 (8)	
O9	−0.0373 (8)	0.7358 (7)	0.8942 (5)	0.0235 (10)	
O1	0.7325 (6)	0.6953 (6)	0.5401 (4)	0.0121 (8)	
C1	0.2683 (8)	0.9145 (8)	0.5903 (6)	0.0108 (10)	
H4	0.3885	1.0063	0.6226	0.013*	
H5	0.1633	0.9841	0.6027	0.013*	
O4	0.0957 (6)	0.6494 (6)	0.6673 (4)	0.0118 (8)	
O8	0.2601 (7)	0.9720 (7)	1.1133 (5)	0.0198 (10)	
N1	0.381 (7)	0.479 (8)	0.070 (5)	0.028 (12)	0.50
H1	0.3025	0.4691	0.1145	0.034*	0.50
C4	0.381 (8)	0.466 (10)	0.078 (5)	0.024 (10)	0.50
H4A	0.3051	0.4405	0.1294	0.029*	0.50
C3	0.5612 (13)	0.5896 (11)	0.1367 (8)	0.0312 (17)	
H3A	0.6025	0.6454	0.2295	0.037*	
C2	0.3206 (12)	0.3837 (11)	−0.0627 (8)	0.0322 (17)	
H2	0.2008	0.3014	−0.1034	0.039*	
O6	0.2543 (6)	0.9385 (6)	0.3492 (4)	0.0133 (8)	
H8	0.193 (16)	0.882 (13)	1.042 (9)	0.06 (3)*	
H7	0.262 (14)	0.950 (13)	1.184 (7)	0.03 (2)*	
H1B	0.844 (10)	0.677 (12)	0.577 (8)	0.03 (2)*	
H1A	0.731 (13)	0.806 (9)	0.573 (8)	0.025*	
H6	−0.032 (11)	0.597 (8)	0.352 (9)	0.03 (3)*	
H9A	0.002 (13)	0.710 (13)	0.828 (8)	0.03 (2)*	
H10	−0.110 (17)	0.817 (16)	0.888 (14)	0.07 (4)*	

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cr1	0.0067 (6)	0.0081 (6)	0.0107 (6)	0.0020 (4)	0.0035 (4)	0.0035 (5)
P2	0.0072 (6)	0.0076 (7)	0.0120 (7)	0.0015 (5)	0.0031 (5)	0.0042 (5)
P1	0.0068 (6)	0.0084 (7)	0.0103 (7)	0.0011 (5)	0.0032 (5)	0.0025 (5)
O2	0.0103 (18)	0.0121 (19)	0.0119 (19)	0.0050 (15)	0.0043 (15)	0.0042 (15)
O5	0.0077 (18)	0.011 (2)	0.019 (2)	0.0004 (15)	0.0019 (15)	0.0053 (16)
O3	0.0110 (18)	0.013 (2)	0.0126 (19)	−0.0004 (15)	0.0036 (15)	0.0006 (16)
O7	0.0103 (18)	0.0116 (19)	0.0136 (19)	0.0046 (15)	0.0047 (15)	0.0048 (15)
O9	0.029 (3)	0.024 (3)	0.021 (2)	0.004 (2)	0.014 (2)	0.007 (2)
O1	0.0082 (18)	0.0088 (19)	0.019 (2)	0.0013 (15)	0.0034 (16)	0.0043 (16)
C1	0.010 (2)	0.008 (2)	0.013 (3)	0.0014 (19)	0.003 (2)	0.003 (2)
O4	0.0085 (18)	0.0114 (19)	0.0153 (19)	0.0000 (14)	0.0039 (15)	0.0043 (15)
O8	0.018 (2)	0.026 (2)	0.013 (2)	−0.0028 (18)	0.0032 (17)	0.0052 (19)
N1	0.04 (2)	0.028 (18)	0.033 (19)	0.019 (13)	0.019 (16)	0.023 (13)
C4	0.026 (18)	0.019 (15)	0.018 (15)	−0.001 (12)	−0.008 (12)	0.008 (13)
C3	0.042 (5)	0.020 (3)	0.021 (3)	0.007 (3)	−0.004 (3)	0.006 (3)
C2	0.033 (4)	0.023 (4)	0.029 (4)	0.000 (3)	−0.008 (3)	0.009 (3)
O6	0.0148 (19)	0.0108 (19)	0.016 (2)	0.0016 (15)	0.0053 (16)	0.0073 (16)

Geometric parameters (Å, °)

Cr1—O1	1.991 (4)	O1—H1B	0.83 (6)
Cr1—O2	1.956 (4)	O1—H1A	0.80 (6)
Cr1—O7	1.964 (4)	C1—H4	0.9700
P2—O6	1.499 (4)	C1—H5	0.9700
P2—O7	1.519 (4)	O8—H8	0.85 (7)
P2—O5	1.568 (4)	O8—H7	0.83 (6)
P2—C1	1.804 (6)	N1—C2	1.34 (5)
P1—O4	1.512 (4)	N1—C3	1.36 (4)
P1—O4	1.512 (4)	N1—H1	0.8600
P1—O2	1.515 (4)	C4—C3	1.40 (5)
P1—O3	1.568 (4)	C4—C2	1.41 (5)
P1—C1	1.797 (6)	C4—H4A	0.9300
O5—H6	0.83 (5)	C3—C2^{i}	1.371 (13)
O3—H3	0.8200	C3—H3A	0.9300
O9—H9A	0.83 (6)	C2—C3^{i}	1.371 (13)
O9—H10	0.84 (7)	C2—H2	0.9300
O2^{ii}—Cr1—O2	180.00 (15)	P2—O5—H6	114 (5)
O2^{ii}—Cr1—O7	88.35 (17)	P1—O3—H3	109.5
O2—Cr1—O7	91.65 (17)	P2—O7—Cr1	140.0 (3)
O2^{ii}—Cr1—O7^{ii}	91.65 (17)	H9A—O9—H10	108 (10)
O2—Cr1—O7^{ii}	88.35 (17)	Cr1—O1—H1B	119 (6)
O7—Cr1—O7^{ii}	180.0 (2)	Cr1—O1—H1A	120 (6)
O2^{ii}—Cr1—O1^{ii}	90.51 (17)	H1B—O1—H1A	107 (9)
O2—Cr1—O1^{ii}	89.49 (17)	P1—C1—P2	114.8 (3)
O7—Cr1—O1^{ii}	90.81 (18)	P1—C1—H4	108.6
O7^{ii}—Cr1—O1^{ii}	89.19 (18)	P2—C1—H4	108.6
O2^{ii}—Cr1—O1	89.49 (17)	P1—C1—H5	108.6
O2—Cr1—O1	90.51 (17)	P2—C1—H5	108.6
O7—Cr1—O1	89.19 (18)	H4—C1—H5	107.5
O7^{ii}—Cr1—O1	90.81 (18)	H8—O8—H7	114 (10)
O1^{ii}—Cr1—O1	180.0 (3)	C2—N1—C3	123 (4)
O6—P2—O7	114.8 (2)	C2—N1—H1	118.3
O6—P2—O5	107.8 (2)	C3—N1—H1	118.3
O7—P2—O5	109.7 (2)	C3—C4—C2	116 (5)
O6—P2—C1	108.2 (3)	C3—C4—H4A	122.1
O7—P2—C1	109.0 (2)	C2—C4—H4A	122.1
O5—P2—C1	107.1 (2)	N1—C3—C2^{i}	118 (2)
O4—P1—O2	115.5 (2)	C2^{i}—C3—C4	122 (3)
O4—P1—O2	115.5 (2)	N1—C3—H3A	121.1
O4—P1—O3	107.9 (2)	C2^{i}—C3—H3A	121.1
O4—P1—O3	107.9 (2)	C4—C3—H3A	116.7
O2—P1—O3	108.6 (2)	N1—C2—C3^{i}	119 (2)

O4—P1—C1	110.1 (2)	C3^{i}—C2—C4	122 (2)
O4—P1—C1	110.1 (2)	N1—C2—H2	120.7
O2—P1—C1	107.6 (2)	C3^{i}—C2—H2	120.7
O3—P1—C1	106.9 (3)	C4—C2—H2	117.1
P1—O2—Cr1	134.1 (2)		

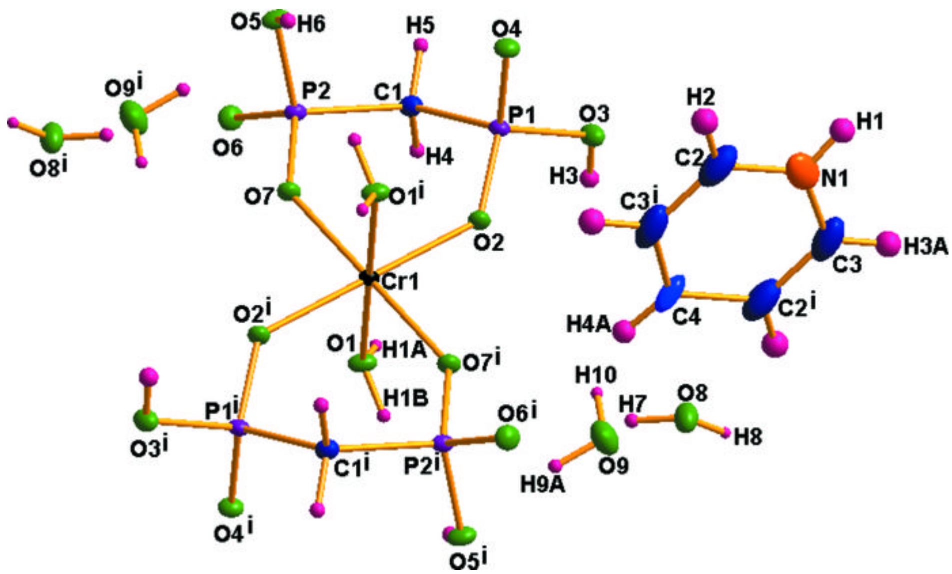
Symmetry codes: (i) −*x*+1, −*y*+1, −*z*; (ii) −*x*+1, −*y*+1, −*z*+1.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H4···O6^{iii}	0.97	2.49	3.346 (7)	147
C4—H4A···O9^{iv}	0.93	2.16	2.93 (7)	140
N1—H1···O9^{iv}	0.86	2.32	3.03 (5)	141
O1—H1A···O6^{iii}	0.80 (6)	1.83 (6)	2.634 (6)	176 (9)
O1—H1B···O4^{v}	0.83 (6)	1.87 (6)	2.704 (6)	177 (9)
O3—H3···O8^{vi}	0.82	1.83	2.629 (6)	163
O5—H6···O4^{iv}	0.83 (5)	1.80 (5)	2.619 (6)	175 (10)
O8—H7···O6^{vii}	0.83 (6)	1.86 (6)	2.687 (6)	171 (9)
O8—H8···O9	0.85 (7)	1.94 (8)	2.748 (7)	158 (11)
O9—H9A···O4	0.83 (6)	2.00 (6)	2.833 (6)	179 (10)
O9—H10···O8^{viii}	0.84 (7)	1.99 (7)	2.820 (7)	174 (13)

Symmetry codes: (iii) −*x*+1, −*y*+2, −*z*+1; (iv) −*x*, −*y*+1, −*z*+1; (v) *x*+1, *y*, *z*; (vi) −*x*+1, −*y*+2, −*z*+2; (vii) *x*, *y*, *z*+1; (viii) −*x*, −*y*+2, −*z*+2.

Fig. 1


O5
H6
H5
O4
O9i
C1
P2
P1
O3
H2
H1
O8i
O6
H4
C2
N1
H3
O7
O1i
C3i
O2
H3A
C3
Cr1
O2i
H4A
C4
C2i
O1
H1A
O7i
H10
H1B
H7
O8
P1i
O6i
H8
O3i
C1i
P2i
O9
H9A
O4i
O5i