metal-organic compounds

Poly[sodium [μ_4-2-hydroxyphosphono-acetato(3−)]iron(II)]

Jing Li, Yan-Yu Zhu, Cui-Ying Huang, Zhen-Gang Sun* and Da-Peng Dong

Institute of Chemistry for Functionalized Materials, College of Chemistry and Chemical Engineering, Liaoning Normal University, Dalian 116029, People's Republic of China
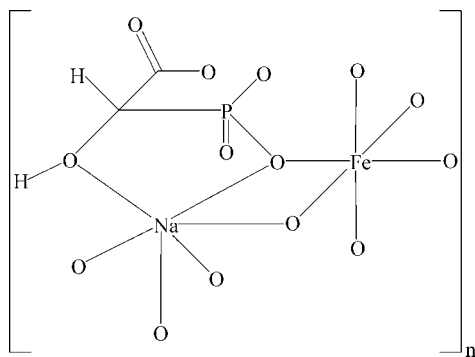Correspondence e-mail: szg188@163.com

The title compound, NaFe[(O$_3$PCH(OH)CO$_2$)] or {Na[Fe-(C$_2$H$_2$O$_6$P)]}$_n$, was synthesized under mild hydrothermal conditions. The Fe^{II} ion is octahedrally coordinated; all O atoms from the 2-hydroxyphosphonoacetate(3−) are involved in metal coordination. The overall structure can be described as a three-dimensional open framework with channels running along the a axis and with the charge‐compensating Na$^+$ cations located inside these channels. This architecture is further stabilized by a number of O—H···O hydrogen bonds involving the protonated hydroxyl O atoms and carboxylate O atoms.

Related literature

For related literature, see: Alberti *et al.* (1999); Clearfield (1996); Fu *et al.* (2005); Odobel *et al.* (2001); Riou *et al.* (1998, 2000).

Experimental

Crystal data

Na[Fe(C$_2$H$_2$O$_6$P)]
M_r = 231.85
Orthorhombic, $Pbca$
a = 10.2676 (8) Å
b = 9.7330 (8) Å
c = 10.8624 (9) Å

V = 1085.53 (15) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 3.12 mm^{-1}
T = 295 (2) K
$0.23 \times 0.17 \times 0.08$ mm

Data collection

Bruker SMART APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
T_{min} = 0.531, T_{max} = 0.795

6143 measured reflections
1309 independent reflections
1213 reflections with $I > 2\sigma(I)$
R_{int} = 0.022

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.022
$wR(F^2)$ = 0.056
S = 1.07
1309 reflections

100 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.50 e Å^{-3}
$\Delta\rho_{min}$ = −0.36 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O4—H4···O5^i	0.88	1.74	2.6168 (19)	173

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

Data collection: *APEX2* (Bruker, 2005); cell refinement: *APEX2*; data reduction: *APEX2*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXTL*.

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supplementary materials

Poly[sodium [μ_4-2-hydroxyphosphonoacetato(3-)]iron(II)]

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Comment

Metal phosphonates with rich composition and structural diversity have attracted considerable attention during the past few years due to their potential applications in catalysis (Clearfield, 1996), ion exchange (Alberti *et al.*, 1999), proton conductivity (Odobel *et al.*, 2001) and gas and liquid separations (Riou *et al.*, 1998,2000). The strategy of attaching additional functional groups such as amine, hydroxyl and carboxylate groups to the phosphonic acid has proven to be effective for the synthesis of metal phosphonates with open-framework and microporous structures. For example, 2-hydroxyphosphonoacetic acid (H_3L) with functional hydroxyl and carboxylate groups is an interesting ligand for the synthesis of metal phosphonates with open-framework structures, since it can adopt various kinds of coordination modes under different reaction conditions which may result in various interesting structures.

The title compound, (I), has been synthesized by hydrothermal technique, using 2-hydroxyphosphonoacetic acid as ligand. Analysis of the single-crystal data reveals that there are one iron(II) ion, one L^{3-} [$L = O_3PCH(OH)CO_2$] ligand, and one Na^+ ion in the asymmetric unit of (I). Each iron(II) ion is octahedrally coordinated by three phosphonate O atoms from three separate L^{3-} ligands (Fig 1) [the Fe—O distance range from 2.032 (1) to 2.196 (1) Å], two carboxylate O atoms from two separate L^{3-} ligands [the Fe—O bond lengths are 2.143 (1) and 2.185 (1) Å] and one hydroxyl O atom [the Fe—O bond length is 2.272 (1) Å]. These values are close to those reported for other analogous six-coordinated iron(II) phosphonates (Fu *et al.*, 2005). As a result, all the O atoms from the L^{3-} ligand are involved in metal coordination, and act as a monodentate connecting one iron(II) ion. The values of the O—Fe—O angles are in the range 69.39 (5)–171.49 (5)°. The overall structure can be described as a three-dimensional open-framework type with channels running along the *a* axis (Fig 2).

Experimental

A mixture of 0.16 g (0.6 mmol) $FeSO_4 \cdot 7H_2O$, 0.5 ml (2.0 mmol) 2-hydroxyphosphonoacetic acid (48.0 wt %) and 0.17 g (4.0 mmol) NaF (as a mineralizer) were dissolved in 10 ml of deionized water, and then 2 mol/*L* NaOH (aq) was added with stirring to adjust the pH of the mixture. The mixture (pH = 4) was sealed in a 20 ml Teflon-lined stainless steel autoclave, and then heated at 433 K for 72 h. Colorless block crystals were obtained, washed with distilled water, and dried in air at room temperature.

Refinement

H atoms were placed in calculated positions and allaowed to ride, with C—H = 0.93 Å or O—H = and $U_{iso}(H) = 1.2U_{eq}(C)$.
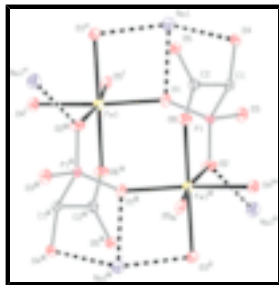
supplementary materials

Figures

Fig. 1. View showing the octahedral coordination of the iron with the atom-labelling scheme. Ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity·[Symmetry codes: (i) $1/2 - x$, $3/2 - y$, $1/2 + z$; (ii) $-x - 1/2$, $3/2 - y$, $1 - z$; (iii) $-x$, $1 - y$, $1 - z$; (iv) $x - 1/2$, y, $1/2 - z$; (v) $1/2 - x$, $y - 1/2$, z].
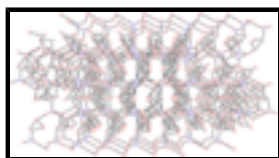

Fig. 2. View of the packing of (I) with the unit cell outlined along the a axis, showing the stacking of compound (I). H and Na atoms have been omitted for clarity.

Poly[sodium [μ$_4$-2-hydroxyphosphonoacetato(3-)]iron(II)]

Crystal data

Na[Fe(C$_2$H$_2$O$_6$P)]	$F_{000} = 912$
$M_r = 231.85$	$D_x = 2.837$ Mg m^{-3}
Orthorhombic, *Pbca*	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
Hall symbol: -P 2ac 2ab	Cell parameters from 3081 reflections
$a = 10.2676$ (8) Å	$\theta = 3.4–28.9º$
$b = 9.7330$ (8) Å	$\mu = 3.12$ mm^{-1}
$c = 10.8624$ (9) Å	$T = 295$ (2) K
$V = 1085.53$ (15) Å^3	Block, colourless
$Z = 8$	$0.23 \times 0.17 \times 0.08$ mm

Data collection

Bruker SMART APEXII CCD diffractometer	1309 independent reflections
Radiation source: fine-focus sealed tube	1213 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.022$
$T = 295(2)$ K	$\theta_{max} = 28.0º$
ω scans	$\theta_{min} = 3.4º$
Absorption correction: empirical (using intensity measurements) (SADABS; Bruker, 2005)	$h = -13 \rightarrow 13$
$T_{min} = 0.531$, $T_{max} = 0.795$	$k = -9 \rightarrow 12$
6143 measured reflections	$l = -14 \rightarrow 11$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map

Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.022$	H-atom parameters constrained
$wR(F^2) = 0.056$	$w = 1/[\sigma^2(F_o^2) + (0.0281P)^2 + 1.0108P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.07$	$(\Delta/\sigma)_{max} = 0.001$
1309 reflections	$\Delta\rho_{max} = 0.50$ e Å^{-3}
100 parameters	$\Delta\rho_{min} = -0.36$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

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

	x	y	z	$U_{iso}*/U_{eq}$
Fe1	0.17708 (3)	0.41645 (3)	0.60678 (3)	0.01090 (10)
P1	0.09669 (4)	0.72190 (5)	0.45975 (5)	0.01002 (12)
Na1	0.37599 (8)	0.58426 (8)	0.42567 (8)	0.01915 (19)
O1	0.17072 (14)	0.60193 (14)	0.51501 (14)	0.0155 (3)
O2	−0.05078 (13)	0.71517 (14)	0.47584 (13)	0.0156 (3)
O3	0.14845 (13)	0.86102 (14)	0.50091 (13)	0.0151 (3)
O4	0.26320 (13)	0.72206 (14)	0.26531 (13)	0.0138 (3)
H4	0.2760	0.8109	0.2565	0.017*
O5	0.18556 (13)	0.48131 (14)	0.22376 (14)	0.0162 (3)
O6	−0.02360 (13)	0.51846 (14)	0.26669 (13)	0.0156 (3)
C1	0.12691 (18)	0.70391 (19)	0.29329 (18)	0.0108 (4)
H1	0.0737	0.7693	0.2466	0.013*
C2	0.09253 (18)	0.5568 (2)	0.25833 (18)	0.0120 (4)

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Fe1	0.00952 (15)	0.01086 (15)	0.01232 (15)	−0.00084 (9)	−0.00043 (10)	0.00006 (10)
P1	0.0097 (2)	0.0090 (2)	0.0113 (2)	−0.00012 (16)	−0.00040 (17)	−0.00060 (17)
Na1	0.0176 (4)	0.0158 (4)	0.0241 (5)	0.0005 (3)	0.0032 (4)	0.0014 (3)
O1	0.0161 (7)	0.0137 (7)	0.0168 (7)	0.0025 (5)	0.0003 (6)	0.0041 (5)
O2	0.0102 (6)	0.0180 (7)	0.0187 (7)	−0.0002 (5)	0.0005 (5)	−0.0056 (5)

O3	0.0168 (7)	0.0114 (7)	0.0170 (7)	−0.0017 (5)	−0.0040 (6)	−0.0014 (5)
O4	0.0126 (6)	0.0097 (6)	0.0189 (7)	−0.0017 (5)	0.0034 (6)	0.0008 (5)
O5	0.0155 (7)	0.0100 (6)	0.0230 (8)	0.0017 (5)	0.0065 (6)	−0.0006 (5)
O6	0.0117 (6)	0.0155 (7)	0.0196 (7)	−0.0020 (5)	0.0006 (5)	−0.0042 (6)
C1	0.0095 (8)	0.0104 (8)	0.0126 (9)	0.0011 (7)	0.0002 (7)	0.0005 (7)
C2	0.0138 (9)	0.0111 (9)	0.0110 (9)	0.0007 (7)	0.0003 (7)	0.0001 (7)

Geometric parameters (Å, °)

Fe1—O2^i	2.0318 (14)	Na1—C2^{vi}	3.002 (2)
Fe1—O1	2.0633 (14)	Na1—P1^v	3.2006 (10)
Fe1—O5^{ii}	2.1434 (14)	Na1—Na1^{vii}	3.4326 (18)
Fe1—O6^i	2.1849 (14)	Na1—Fe1^{viii}	3.5065 (10)
Fe1—O3^{iii}	2.1960 (14)	O2—Fe1^i	2.0318 (14)
Fe1—O4^{ii}	2.2713 (14)	O2—Na1^{iv}	2.3497 (16)
Fe1—Na1	3.2725 (9)	O3—Fe1^{ix}	2.1960 (14)
Fe1—Na1^{ii}	3.5065 (10)	O3—Na1^{ix}	2.3349 (16)
P1—O1	1.5171 (14)	O3—Na1^{iv}	2.9574 (17)
P1—O3	1.5218 (14)	O4—C1	1.443 (2)
P1—O2	1.5256 (14)	O4—Fe1^{viii}	2.2713 (14)
P1—C1	1.843 (2)	O4—H4	0.8797
P1—Na1	3.1868 (10)	O5—C2	1.262 (2)
P1—Na1^{iv}	3.2006 (10)	O5—Fe1^{viii}	2.1434 (14)
Na1—O1	2.3267 (17)	O6—C2	1.253 (2)
Na1—O3^{iii}	2.3349 (16)	O6—Fe1^i	2.1849 (14)
Na1—O2^v	2.3497 (16)	O6—Na1^x	2.4164 (17)
Na1—O6^{vi}	2.4164 (17)	C1—C2	1.523 (3)
Na1—O4	2.4848 (16)	C1—H1	0.9800
Na1—O3^v	2.9574 (17)	C2—Na1^x	3.002 (2)
O2^i—Fe1—O1	108.55 (6)	O3^{iii}—Na1—P1^v	119.24 (5)
O2^i—Fe1—O5^{ii}	167.05 (6)	O2^v—Na1—P1^v	26.70 (3)
O1—Fe1—O5^{ii}	84.32 (6)	O6^{vi}—Na1—P1^v	100.98 (4)
O2^i—Fe1—O6^i	90.02 (5)	O4—Na1—P1^v	106.52 (4)
O1—Fe1—O6^i	91.57 (6)	O3^v—Na1—P1^v	28.26 (3)
O5^{ii}—Fe1—O6^i	88.11 (5)	C2^{vi}—Na1—P1^v	77.70 (4)
O2^i—Fe1—O3^{iii}	97.73 (5)	P1—Na1—P1^v	110.13 (2)
O1—Fe1—O3^{iii}	89.30 (5)	O1—Na1—Fe1	38.81 (4)
O5^{ii}—Fe1—O3^{iii}	83.55 (5)	O3^{iii}—Na1—Fe1	42.10 (4)
O6^i—Fe1—O3^{iii}	171.49 (5)	O2^v—Na1—Fe1	109.92 (5)
O2^i—Fe1—O4^{ii}	97.64 (5)	O6^{vi}—Na1—Fe1	130.83 (5)
O1—Fe1—O4^{ii}	153.40 (6)	O4—Na1—Fe1	113.58 (4)
O5^{ii}—Fe1—O4^{ii}	69.42 (5)	O3^v—Na1—Fe1	121.21 (4)
O6^i—Fe1—O4^{ii}	83.68 (5)	C2^{vi}—Na1—Fe1	144.90 (5)

O3^{iii}—Fe1—O4^{ii}	91.78 (5)	P1—Na1—Fe1	65.06 (2)
O2^{i}—Fe1—Na1	116.58 (5)	P1^{v}—Na1—Fe1	120.15 (3)
O1—Fe1—Na1	44.98 (4)	O1—Na1—Na1^{vii}	120.74 (6)
O5^{ii}—Fe1—Na1	73.38 (4)	O3^{iii}—Na1—Na1^{vii}	58.02 (4)
O6^{i}—Fe1—Na1	133.12 (4)	O2^{v}—Na1—Na1^{vii}	86.87 (5)
O3^{iii}—Fe1—Na1	45.47 (4)	O6^{vi}—Na1—Na1^{vii}	87.91 (5)
O4^{ii}—Fe1—Na1	125.70 (4)	O4—Na1—Na1^{vii}	158.98 (6)
O2^{i}—Fe1—Na1^{ii}	109.63 (4)	O3^{v}—Na1—Na1^{vii}	42.05 (3)
O1—Fe1—Na1^{ii}	118.30 (5)	C2^{vi}—Na1—Na1^{vii}	73.81 (5)
O5^{ii}—Fe1—Na1^{ii}	61.15 (4)	P1—Na1—Na1^{vii}	144.47 (5)
O6^{i}—Fe1—Na1^{ii}	42.87 (4)	P1^{v}—Na1—Na1^{vii}	64.75 (3)
O3^{iii}—Fe1—Na1^{ii}	130.06 (4)	Fe1—Na1—Na1^{vii}	86.66 (3)
O4^{ii}—Fe1—Na1^{ii}	44.91 (4)	O1—Na1—Fe1^{viii}	105.75 (5)
Na1—Fe1—Na1^{ii}	133.773 (18)	O3^{iii}—Na1—Fe1^{viii}	109.10 (5)
O1—P1—O3	113.18 (8)	O2^{v}—Na1—Fe1^{viii}	120.07 (5)
O1—P1—O2	114.76 (8)	O6^{vi}—Na1—Fe1^{viii}	37.96 (3)
O3—P1—O2	110.56 (8)	O4—Na1—Fe1^{viii}	40.19 (3)
O1—P1—C1	103.34 (8)	O3^{v}—Na1—Fe1^{viii}	114.44 (4)
O3—P1—C1	108.30 (8)	C2^{vi}—Na1—Fe1^{viii}	57.12 (4)
O2—P1—C1	105.99 (8)	P1—Na1—Fe1^{viii}	88.61 (2)
O1—P1—Na1	43.24 (6)	P1^{v}—Na1—Fe1^{viii}	119.69 (3)
O3—P1—Na1	95.39 (6)	Fe1—Na1—Fe1^{viii}	119.73 (3)
O2—P1—Na1	152.67 (6)	Na1^{vii}—Na1—Fe1^{viii}	125.38 (4)
C1—P1—Na1	72.21 (6)	P1—O1—Fe1	151.70 (9)
O1—P1—Na1^{iv}	130.89 (6)	P1—O1—Na1	110.23 (8)
O3—P1—Na1^{iv}	66.95 (6)	Fe1—O1—Na1	96.21 (6)
O2—P1—Na1^{iv}	43.78 (6)	P1—O2—Fe1^{i}	127.58 (8)
C1—P1—Na1^{iv}	123.83 (6)	P1—O2—Na1^{iv}	109.52 (7)
Na1—P1—Na1^{iv}	158.45 (2)	Fe1^{i}—O2—Na1^{iv}	121.38 (7)
O1—Na1—O3^{iii}	79.95 (5)	P1—O3—Fe1^{ix}	131.10 (8)
O1—Na1—O2^{v}	92.21 (6)	P1—O3—Na1^{ix}	133.44 (8)
O3^{iii}—Na1—O2^{v}	130.40 (7)	Fe1^{ix}—O3—Na1^{ix}	92.43 (6)
O1—Na1—O6^{vi}	140.06 (6)	P1—O3—Na1^{iv}	84.78 (6)
O3^{iii}—Na1—O6^{vi}	95.85 (6)	Fe1^{ix}—O3—Na1^{iv}	125.89 (6)
O2^{v}—Na1—O6^{vi}	118.51 (6)	Na1^{ix}—O3—Na1^{iv}	79.93 (5)
O1—Na1—O4	80.23 (5)	C1—O4—Fe1^{viii}	110.42 (10)
O3^{iii}—Na1—O4	134.23 (6)	C1—O4—Na1	103.78 (10)
O2^{v}—Na1—O4	91.14 (5)	Fe1^{viii}—O4—Na1	94.89 (5)
O6^{vi}—Na1—O4	74.68 (5)	C1—O4—H4	106.7
O1—Na1—O3^{v}	136.98 (6)	Fe1^{viii}—O4—H4	117.4
O3^{iii}—Na1—O3^{v}	100.07 (5)	Na1—O4—H4	122.5

O2^v—Na1—O3^v	54.89 (5)	C2—O5—Fe1^{viii}	113.84 (12)
O6^{vi}—Na1—O3^v	82.95 (5)	C2—O6—Fe1^i	130.23 (13)
O4—Na1—O3^v	122.19 (5)	C2—O6—Na1^x	105.34 (12)
O1—Na1—C2^{vi}	162.81 (7)	Fe1^i—O6—Na1^x	99.17 (6)
O3^{iii}—Na1—C2^{vi}	103.28 (6)	O4—C1—C2	106.71 (14)
O2^v—Na1—C2^{vi}	98.06 (6)	O4—C1—P1	111.00 (12)
O6^{vi}—Na1—C2^{vi}	23.73 (5)	C2—C1—P1	107.16 (13)
O4—Na1—C2^{vi}	85.79 (5)	O4—C1—H1	110.6
O3^v—Na1—C2^{vi}	59.66 (5)	C2—C1—H1	110.6
O1—Na1—P1	26.53 (4)	P1—C1—H1	110.6
O3^{iii}—Na1—P1	104.70 (5)	O6—C2—O5	124.66 (18)
O2^v—Na1—P1	83.44 (4)	O6—C2—C1	118.85 (17)
O6^{vi}—Na1—P1	126.57 (5)	O5—C2—C1	116.49 (16)
O4—Na1—P1	55.61 (4)	O6—C2—Na1^x	50.93 (10)
O3^v—Na1—P1	138.09 (4)	O5—C2—Na1^x	114.47 (13)
C2^{vi}—Na1—P1	141.39 (5)	C1—C2—Na1^x	104.71 (11)
O1—Na1—P1^v	115.82 (5)		

Symmetry codes: (i) $-x$, $-y+1$, $-z+1$; (ii) $-x+1/2$, $-y+1$, $z+1/2$; (iii) $-x+1/2$, $y-1/2$, z; (iv) $x-1/2$, $-y+3/2$, $-z+1$; (v) $x+1/2$, $-y+3/2$, $-z+1$; (vi) $x+1/2$, y, $-z+1/2$; (vii) $-x+1$, $-y+1$, $-z+1$; (viii) $-x+1/2$, $-y+1$, $z-1/2$; (ix) $-x+1/2$, $y+1/2$, z; (x) $x-1/2$, y, $-z+1/2$.

Hydrogen-bond geometry (Å, °)

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
O4—H4⋯O5^{ix}	0.88	1.74	2.6168 (19)	173

Symmetry codes: (ix) $-x+1/2$, $y+1/2$, z.

Fig. 1

Fig. 2