

Layered poly[μ_2 -aqua- μ_3 -dimethylformamide-di- μ_3 -phenylphosphonato-dipotassium]Márcia R. Siquiera,^a Janaina T. Facco,^a Ernesto S. Lang,^a Fabiane Lorenzini,^b Mara R. Rizzatti,^b Javier Ellena^c and Robert A. Burrow^{a*}

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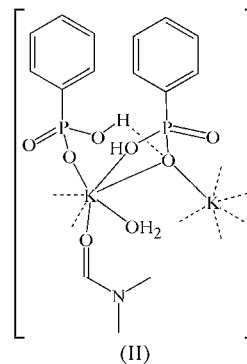
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The first structurally characterized alkali metal phosphonate, the title compound, $[K_2(C_6H_6O_3P)_2(C_3H_7NO)(H_2O)]_n$, has a complex structure, with layers parallel to the crystallographic *bc* plane consisting of two crystallographically independent K atoms sandwiched between the three types of ligands present in the structure, *viz.* water molecules, dimethylformamide molecules and two crystallographically independent phenylphosphonate ligands. Six O atoms coordinate to one K atom and seven to the other. The interlayer distance is 15.327 (4) Å. The K—O distances are in the range 2.739 (2)–2.932 (2) Å for the seven-coordinate K atom and 2.650 (2)–2.821 (2) Å for the six-coordinate K atom.

Comment

Metal phosphonates have been much used as inorganic-organic hybrid materials because of their potential applications (Clearfield, 1996, 2002). Complexes with metal ions frequently form laminar structures in the solid state that consist of $PO_3 \cdots M \cdots O_3P$ layers separated by the organic groups (Vioux *et al.*, 2004). The phosphonate group permits flexibility in the construction of solids, with the possibility of forming strong hydrogen bonds between the hydroxy groups and terminal O atoms (Mahmoudkhani & Langer, 2002). Complexes with a variety of metal centres (alkaline earth, transition, main group or lanthanide, usually in the +2 to +4 oxidation state) have been studied (Cao *et al.*, 1988, 1990; Poojary *et al.*, 1996; Mahmoudkhani & Langer, 2001; Mahmoudkhani *et al.*, 2002). However, until now, no structure of a phosphonate complex with a monovalent metal ion has been reported. The only similar complex whose structure has been reported is aquapyrazole-4-sulfonatepotassium (Mezei & Raptis, 2003). The sulfonate group, SO_3^- , has a structure

similar to that of the phosphonate group but forms much weaker bonds to metal atoms (Côté & Shimizu, 2003).



The fact that alkali and alkaline earth metals have a rich coordination chemistry with O-atom donor ligands (Poonia & Bajaj, 1979) prompted us to study their phosphinate complexes. In the case of potassium phenylphosphinate, accidental air oxidation of the anion during the preparation led to the formation of potassium phenylphosphonate, (I). Repetition of the synthesis with hydrogen peroxide as the oxidation agent led to the pure product. A differential scanning calorimetry analysis of (I) showed no peaks in the range 323–623 K, demonstrating the thermal robustness of the compound. A sample of (I) prepared in methanol showed good crystallinity [$T_m = 585.5$ K, $\Delta H_m = 66.8$ J g⁻¹ and $T_c =$

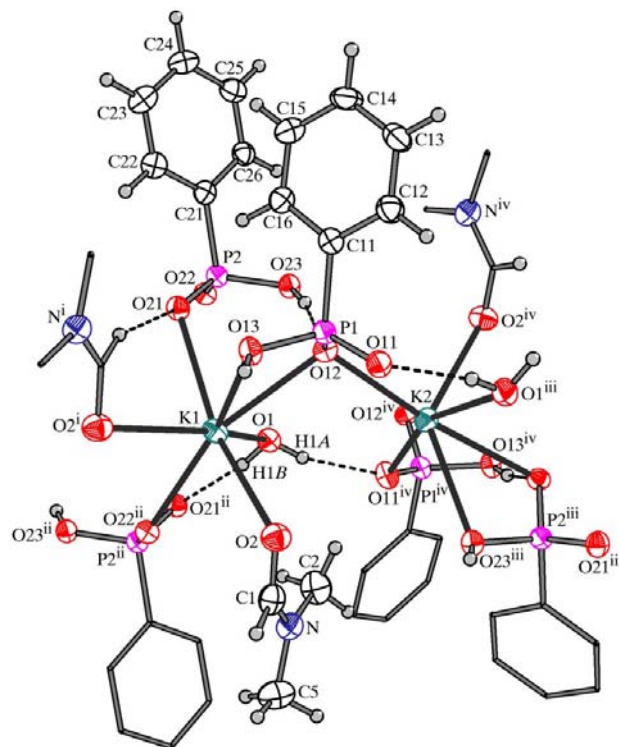


Figure 1

An ORTEP-3 (Farrugia, 1997) representation (50% probability displacement ellipsoids) of the asymmetric unit of (II), showing the coordination geometry around the K atoms. Further residues are included to complete the coordination spheres but are simplified for clarity. [Symmetry codes: (i) $1 - x, 2 - y, 1 - z$; (ii) $1 - x, 1 - y, 1 - z$; (iii) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$; (iv) $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$.

512.6 K, $\Delta H_c = -24.3 \text{ J g}^{-1}$]. Crystallization of (I), by slow evaporation of an aqueous dimethylformamide solution of potassium phenylphosphonate in a desiccator, produced good quality plate-like crystals of the title compound, (II)

A view of the asymmetric unit is given in Fig. 1, and Table 1 lists selected distances and angles. The extended structure of (II) consists of complex layers parallel to the crystallographic *bc* plane, the interlayer distance being 15.327 (4) Å. Layers consisting of two crystallographically independent K atoms lie between double layers of the ligands (water, dimethylformamide and two crystallographically independent phenylphosphonate ligands), which form bonds to the K atoms *via* their O atoms. An extensive network of hydrogen bonds (Table 2) is observed. An approximately square two-dimensional net is formed, with chains of phosphonate ligands parallel to the *b* axis linked by hydrogen bonding between their hydroxy H atoms and negatively charged O atoms, and interconnected in the crystallographic *c* direction by hydrogen bonds between the doubly bonded O atoms and water H atoms (Fig. 2). The packing is shown in Fig. 3.

The potassium centres in (II) exhibit very different coordination geometries. Most of the K—O distances are slightly longer than the sum of the covalent radii (2.69 Å; Allen *et al.*, 1987) but may be considered weak ionic bonds because of their directionality; other K—O interactions are considerably longer. Atom K1 is seven-coordinate, with an approximately pentagonal-bipyramidal coordination geometry. Atoms O2 from a dimethylformamide molecule and O21 from a

phenylphosphonate ligand occupy the apical positions. Atoms O12 and O13 from a chelating phenylphosphonate ligand, O2(1 - *x*, *y* - ½, ½ - *z*) from a symmetry-related dimethylformamide molecule, O1 from a bridging water molecule, and O22(1 - *x*, 1 - *y*, 1 - *z*), a bridging O atom from a symmetry-related phenylphosphonate ligand, occupy the equatorial positions. The K1—O distances are in the range 2.739 (2)–2.932 (2) Å, in agreement with the average K—O distance for KO₇ moieties in the Cambridge Structural Database [CSD; 2.80 (11) Å for 446 observations; Allen, 2002]. The next longest (non-bonded) interaction is 3.544 (4) Å [K1···O1ⁱⁱ; symmetry code: (ii) -*x* + 1, -*y* + 1, -*z* + 1].

Atom K2 is six-coordinate, with atoms O12 and O11^{iv} from two different phenylphosphonate ligands, O22ⁱⁱⁱ and O23ⁱⁱⁱ from a chelating phenylphosphonate ligand, and O1ⁱⁱⁱ and O2^{iv} from bridging water and dimethylformamide molecules, respectively, making up the primary coordination environment [symmetry codes: (iii) -*x* + 1, *y* + ½, -*z* + ½; (iv) -*x* + 1, *y* - ½, -*z* + ½]. The geometry is far from regular octahedral because of the small bite angle of the chelating phenylphosphonate group; the O22ⁱⁱⁱ—K2—O23ⁱⁱⁱ angle is 52.46 (6)°. The K2—O distances are in the range 2.650 (2)–2.821 (2) Å, similar to the average for KO₆ groups found in the CSD [2.80 (9) Å for 1506 observations]. The next longest K2···O non-bonded interaction is to atom O11, at 3.491 (4) Å. The

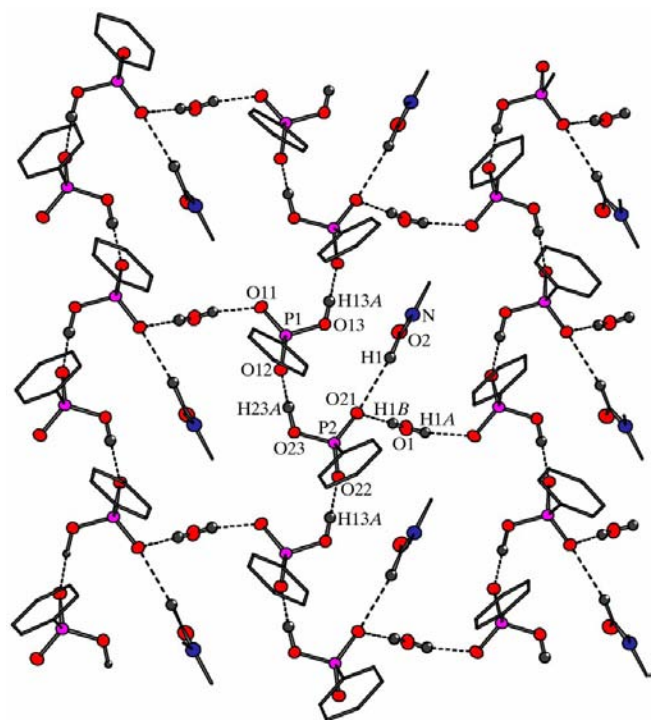


Figure 2
A view of the two-dimensional net in (II), showing hydrogen bonding between the phenylphosphonate ligands and the dimethylformamide and water molecules. The vertical direction is parallel to the *b* axis and the horizontal direction is parallel to the *c* axis. Phenyl C atoms are shown as lines.

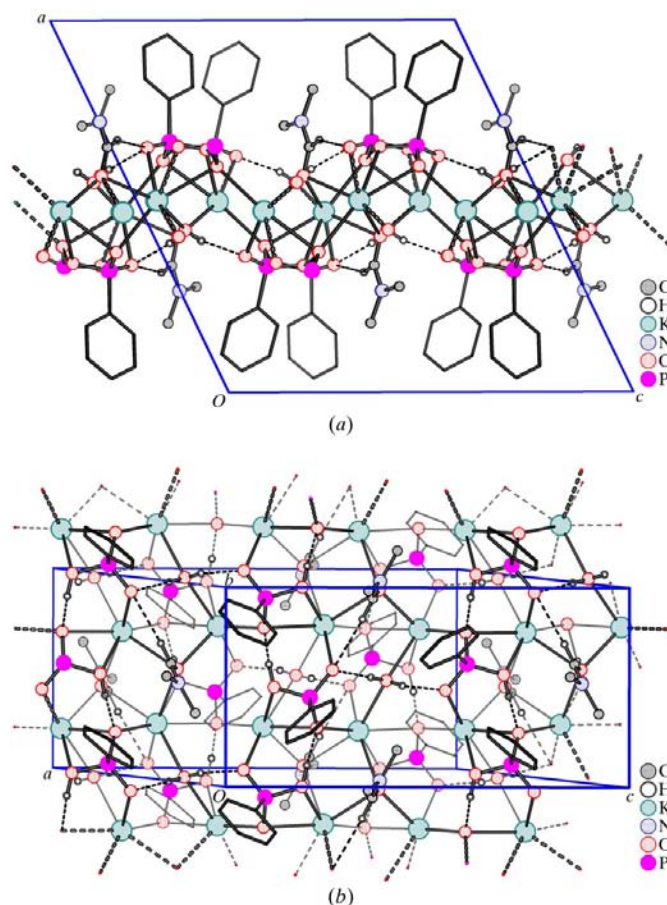


Figure 3
Views (a) perpendicular and (b) parallel to the *bc* plane of the polymeric structure of (II). Phenyl C atoms are shown as lines.

closest distance between K atoms is 3.9769 (15) Å [K1...K2^v; symmetry code: (v) $x, -y + \frac{3}{2}, z + \frac{1}{2}$].

The geometries of the phenylphosphonate ligands are very similar, the two ligands forming similar bonds *via* their O atoms to the K atoms, creating a system of bridges between the metal atoms that extends in the crystal in two dimensions. Each of the two phenylphosphinate ligands exhibits three different P—O distances, with one long distance, associated with the bond to the hydroxy group, and two much shorter distances, the slightly longer of which can be attributed to the bond to the negatively charged O atom and the other to the doubly bonded O atom. The small differences [0.022 (3) and 0.020 (3) Å for atoms P1 and P2, respectively] between the bonds to the negatively charged (P—O1) and doubly bonded O atoms (P—O2) is common for phosphonate ligands bound to metal centres. The median difference for similar phosphonates in the CSD is 0.016 Å (86 observations). The two ligands bind in the same fashion to the potassium centres, chelating one metal centre *via* the hydroxy and negatively charged O atoms (the latter also forms a bifurcated bond to another metal centre), and forming a bond between the doubly bound O atom and another metal centre.

The water molecules form symmetric bridges between atoms K1 and K2, with additional hydrogen-bond interactions to atoms O21 and O11. The O atom of the dimethylformamide molecule exhibits interactions to three K atoms, with a closer interaction to K2 and two longer distances to K1. A hydrogen bond from the C1—H1 group to atom O22(1 - x , 2 - y , 1 - z) of a neighbouring phosphonate group is also observed.

Experimental

Compound (I) was synthesized by dissolving K₂CO₃ (0.200 g, 1.447 mmol) in distilled water (30 ml) and then adding phenylphosphinic acid (0.411 g, 2.892 mmol). To the clear and colourless solution, hydrogen peroxide (10%, 10 ml) was added and the solution was refluxed for 2 h. The water was removed under vacuum to give a white powder (yield 0.447 g, 78.9%). *Caution:* concentrated hydrogen peroxide is explosive in the presence of bases. Crystals of (II) were formed by the slow evaporation of a solution of (I) in a mixture of dimethylformamide and water (1:1 *v/v*) in a desiccator. Analysis found: C 36.73, H 4.80, N 2.68%; calculated: C 37.26, H 4.38, N 2.90%.

Crystal data

[K ₂ (C ₆ H ₆ O ₃ P) ₂ (C ₃ H ₇ NO)(H ₂ O)]	$D_x = 1.52 \text{ Mg m}^{-3}$
$M_r = 483.47$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 16 207 reflections
$a = 16.988 (5) \text{ \AA}$	$\theta = 0.4\text{--}26.0^\circ$
$b = 8.264 (5) \text{ \AA}$	$\mu = 0.64 \text{ mm}^{-1}$
$c = 16.684 (5) \text{ \AA}$	$T = 153 (2) \text{ K}$
$\beta = 115.545 (5)^\circ$	Plate, colourless
$V = 2113.3 (16) \text{ \AA}^3$	$0.14 \times 0.12 \times 0.08 \text{ mm}$
$Z = 4$	

Data collection

Nonius KappaCCD diffractometer	2927 reflections with $I > 2\sigma(I)$
φ scans	$R_{\text{int}} = 0.082$
Absorption correction: multi-scan (Blessing, 1995)	$\theta_{\text{max}} = 26.0^\circ$
$T_{\text{min}} = 0.901, T_{\text{max}} = 0.951$	$h = -20 \rightarrow 20$
25 724 measured reflections	$k = -10 \rightarrow 10$
4152 independent reflections	$l = -20 \rightarrow 18$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.044$
 $wR(F^2) = 0.116$
 $S = 1.06$
 4152 reflections
 270 parameters

H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0612P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.33 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.45 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

K1—O1	2.740 (3)	P1—O11	1.491 (2)
K1—O2	2.925 (3)	P1—O12	1.513 (2)
K1—O2 ⁱ	2.932 (2)	P1—O13	1.578 (2)
K1—O12	2.831 (2)	P2—O21	1.499 (2)
K1—O13	2.900 (2)	P2—O22	1.513 (2)
K1—O21	2.822 (2)	P2—O23	1.579 (2)
K1—O22 ⁱⁱ	2.739 (2)	O2—C1	1.250 (4)
K2—O1 ⁱⁱⁱ	2.734 (2)	C1—N	1.331 (4)
K2—O2 ^{iv}	2.772 (2)	N—C5	1.450 (4)
K2—O11 ^{iv}	2.650 (2)	N—C2	1.449 (4)
K2—O12	2.681 (2)	K1...K1 ⁱ	4.143 (3)
K2—O22 ⁱⁱⁱ	2.821 (2)	K1...K2 ^v	3.9769 (15)
K2—O23 ⁱⁱⁱ	2.800 (2)	K2...K2 ^{iv}	4.558 (2)
O11—P1—O12	116.09 (12)	O21—P2—O22	116.87 (11)
O11—P1—O13	111.11 (12)	O21—P2—O23	111.18 (11)
O12—P1—O13	106.22 (11)	O22—P2—O23	106.94 (11)

Symmetry codes: (i) $-x + 1, -y + 2, -z + 1$; (ii) $-x + 1, -y + 1, -z + 1$; (iii) $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$; (iv) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$; (v) $x, -y + \frac{3}{2}, z + \frac{1}{2}$.

Table 2

Hydrogen-bond geometry (Å, °).

$D\text{—}H\cdots A$	$D\text{—}H$	$H\cdots A$	$D\cdots A$	$D\text{—}H\cdots A$
O1—H1A...O11 ^{iv}	0.82 (4)	1.91 (4)	2.711 (3)	164 (4)
O1—H1B...O21 ⁱⁱ	0.85 (3)	1.85 (4)	2.686 (3)	169 (3)
O13—H13A...O22 ^{vi}	0.92 (3)	1.67 (3)	2.573 (3)	169 (3)
O23—H23A...O12	0.98 (3)	1.61 (3)	2.566 (3)	164 (3)
C1—H1...O21 ⁱ	0.99 (3)	2.47 (3)	3.393 (4)	156 (3)

Symmetry codes: (i) $-x + 1, -y + 2, -z + 1$; (ii) $-x + 1, -y + 1, -z + 1$; (iv) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$; (vi) $x, y + 1, z$.

All H atoms were located in a difference Fourier map. Phenyl H atoms were placed at idealized positions, with C—H distances of 0.95 Å, and refined using a riding model, with $U_{\text{iso}}(\text{H})$ values of $1.2U_{\text{eq}}(\text{C})$. Methyl H atoms were positioned by a best fit to the Fourier peaks, with C—H distances of 0.98 Å, and refined as idealized rigid groups allowed to rotate but not tip, with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$. Atom H1 was refined freely, with a $U_{\text{iso}}(\text{H})$ value of $1.2U_{\text{eq}}(\text{C})$, and the hydroxy and water H atoms were also refined freely, with $U_{\text{iso}}(\text{H})$ values of $1.5U_{\text{eq}}(\text{O})$.

Data collection: COLLECT (Nonius, 2000); cell refinement: SCALEPACK (Otwinowski & Minor, 1997); data reduction: DENZO (Otwinowski & Minor, 1997) and SCALEPACK; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 for Windows (Farrugia, 1997); software used to prepare material for publication: WinGX (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1691). Services for accessing these data are described at the back of the journal.

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