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Dipotassium nickel(II) bis(dihydrogendiphosphate) dihydrate, $K_2Ni(H_2P_2O_7)_2\cdot 2H_2O$

Aziz Alaoui Tahiri,[a] Ibtissam Messouri,[a] Mohammed Lachkar,[a] Peter Y. Zavalij,[b] Robert Glaum,[c] Brahim El Bali[a]* and Ouarsal Rachid[a]

[a]Département de Chimie, Faculté des Sciences Dhar Mehraz, BP 1796 Atlas, 30000 Fès, Morocco, [b]Institute for Materials Research and Department of Chemistry, State University of New York at Binghamton, NY 13902-6000, USA, and [c]Institut für Anorganische Chemie, Universität Bonn, Gerhard-Domagk-Straße 1, D-53121 Bonn, Germany

Correspondence e-mail:
belbali@eudoramail.com

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(P–O) = 0.003 Å
R factor = 0.044
wR factor = 0.099
Data-to-parameter ratio = 14.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

$K_2Ni(H_2P_2O_7)_2\cdot 2H_2O$ is isostructural with its Zn analogue. Its structure is characterized by $[Ni(H_2O)_2(H_2P_2O_7)_2]^{2-}$coordination units. These are linked by hydrogen bonds and K^+ ions. Ni^{2+} is situated on an inversion centre and has an almost regular octahedral coordination.

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Comment

The present work is a continuation of our investigation of the series $A_xT_y(H_2P_2O_7)_z\cdot nH_2$O ($A$ = alkali metal, T = transition metal or magnesium). We previously reported three compounds of this family of acid pyrophosphates for A = K and n = 2, *viz.* T = Co (Alaoui *et al.*, 2002), Zn (Alaoui *et al.*, 2003*a*), and recently Mn (Alaoui *et al.*, 2003*b*). $K_2Ni(H_2P_2O_7)_2\cdot 2H_2O$ is isotypic with the zinc compound.

The crystal structure of the new dihydrogenpyrophosphate (Fig. 1) can be described as a three-dimensional network built of $[Ni(H_2O)_2(H_2P_2O_7)_2]^{2-}$ coordination units, which are linked by potassium ions and hydrogen bonds.

The potassium ions are coordinated by seven O atoms. Distances d(K—O) < 3.15 Å (the shortest K···H distance) are regarded as contributing to the bonding around potassium. Fig. 1 shows a projection on to the *ac* plane of the structure of $K_2Ni(H_2P_2O_7)_2\cdot 2H_2O$.

The unit cell contains two unique P atoms coordinated by four O atoms in a slightly distorted tetrahedral conformation. The two tetrahedra share one corner (O1) to form the pyrophosphate unit. The average distance in the P_2O_7 group is

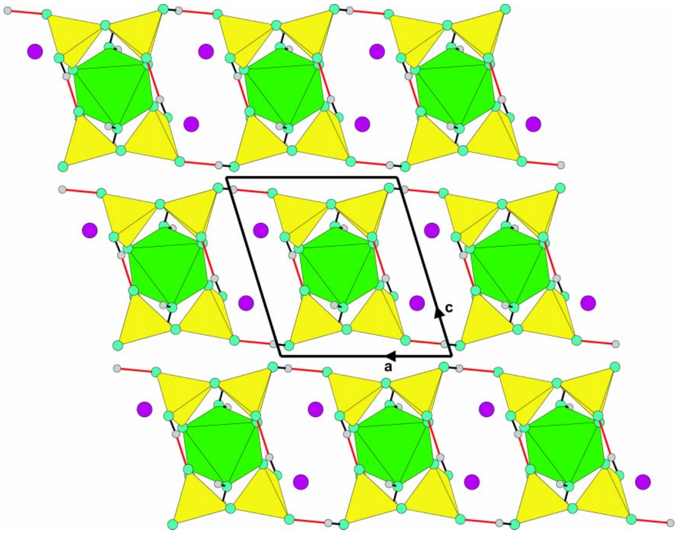

Figure 1
Projection of the crystal structure along the b axis, including hydrogen bonding (red lines). Key: polyhedra: yellow (P_2O_7, green (NiO_6); balls: large pink (K), small grey (H), small blue (O).

d_{av}(P—O) = 1.537 Å. This value is almost identical to those found in other acid pyrophosphates $K_2T(H_2P_2O_7)_2·2H_2O$ [T = Mn (1.534 Å), Co (1.538 Å) and Zn (1.533 Å)]. As in other compounds with the same formula type, the [$H_2P_2O_7$] groups in $K_2Ni(H_2P_2O_7)_2·2H_2O$ show, due to the chelating bonding mode to Ni^{2+}, an almost eclipsed conformation with an O—P—O bridging angle of 130.1 (2)°. This value is close to those reported for the Mn and Zn compounds, respectively, *viz*. 130.9 (2) and 130.8 (2)°.

The environment of the nickel cations in $K_2Ni(H_2P_2O_7)_2·2H_2O$ consists of two bidendate dihydrogenpyrophosphate moieties and two water molecules. Ni^{2+} has an almost regular octahedral coordination with d_{av}(Ni—O) = 2.058 Å. This value is close to those observed for [NiO_6] in anhydrous phosphates (α-$Ni_2P_2O_7$ (2.077 Å; Lukaszewicz, 1967), $Ni_2P_4O_{12}$ (2.045 Å; Nord, 1983) and $SrNi_2(PO_4O)_2$ (2.077 Å; El Bali *et al.*, 1993).

In Fig. 2, the oxygen coordination around K, Ni and P is illustrated.

Another characteristic feature of this structure involves hydrogen bonding of the H atoms of the [$H_2P_2O_7$] groups and of the water molecules to terminal atoms of the pyrophosphate groups, interconnecting the coordination units $[Ni(H_2O)_2(H_2P_2O_7)_2]^{2-}$ into a three-dimensional network (Fig. 1).

Experimental

Crystals were prepared by dissolving $NiCl_2·6H_2O$ in a solution of $K_4P_2O_7$ in water. The mixture was stirred for 1 d and the resulting green solution was allowed to stand at room temperature. After a few days, small pale-green crystals deposited, which were filtered off and washed with 80% ethanol solution.

Crystal data

$K_2Ni_2(H_2P_2O_7)_2·2H_2O$
M_r = 524.85
Triclinic, $P\overline{1}$
a = 6.8554 (8) Å
b = 7.3124 (9) Å
c = 7.5610 (9) Å
α = 81.012 (2)°
β = 72.301 (2)°
γ = 83.691 (2)°
V = 355.87 (7) Å^3
Z = 1
D_x = 2.449 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1086 reflections
θ = 2.8–28.8°
μ = 2.48 mm^{-1}
T = 293 (2) K
Needle, pale green
0.28 × 0.06 × 0.05 mm

Data collection

Bruker SMART APEX diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.692, T_{max} = 0.883
3793 measured reflections
1757 independent reflections
1290 reflections with $I > 2\sigma(I)$
R_{int} = 0.046
θ_{max} = 28.3°
h = −9 → 9
k = −9 → 9
l = −10 → 10

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.099
S = 0.96
1757 reflections
123 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.045P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ < 0.001
$\Delta\rho_{max}$ = 0.56 e Å^{-3}
$\Delta\rho_{min}$ = −0.54 e Å^{-3}

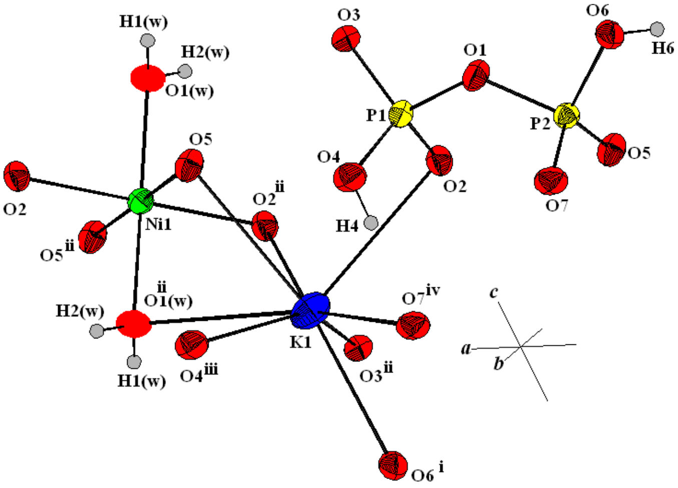

Figure 2
Coordination of K, Ni and P, with anisotropic displacement parameters drawn at the 50% probability level. Key: green (Ni), blue (K), red (O), yellow (P), grey (H). [Symmetry codes: (i) $x, y, 1 + z$; (ii) $1 - x, 1 - y, 1 - z$; (iii) $1 - x, y, 1 - z$; (iv) $2 - x, y, 1 - z$; (v) $1 + x, y, z$.]

Table 1
Selected geometric parameters (Å, °).

K—O6^{i}	2.761 (3)	Ni—O1W	2.067 (3)
K—O2^{ii}	2.788 (3)	P1—O2	1.495 (3)
K—O4^{iii}	2.869 (3)	P1—O3	1.495 (3)
K—O7^{iv}	2.924 (3)	P1—O4	1.556 (3)
K—O1W^{ii}	2.958 (3)	P1—O1	1.602 (3)
K—O5	2.960 (3)	P2—O7	1.501 (3)
K—O2^{v}	3.149 (3)	P2—O5	1.502 (3)
K—O3^{ii}	3.311 (3)	P2—O6	1.542 (3)
Ni—O5	2.052 (3)	P2—O1	1.604 (3)
Ni—O2	2.055 (3)		
O2—P1—O3	116.38 (16)	O7—P2—O5	114.66 (17)
O2—P1—O4	110.01 (17)	O7—P2—O6	111.44 (17)
O3—P1—O4	109.28 (16)	O5—P2—O6	112.52 (17)
O2—P1—O1	109.40 (15)	O7—P2—O1	107.50 (16)
O3—P1—O1	104.78 (15)	O5—P2—O1	110.49 (15)
O4—P1—O1	106.44 (16)	O6—P2—O1	98.98 (16)

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

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

D—H···A	D—H	H···A	D···A	D—H···A
O4—H4···O7^{iii}	0.79 (3)	1.74 (3)	2.530 (4)	175 (5)
O6—H6···O3^{v}	0.78 (3)	1.75 (3)	2.522 (4)	169 (6)
O1W—H1W···O3^{vi}	0.79 (3)	1.97 (3)	2.746 (4)	169 (5)
O1W—H2W···O7^{vii}	0.77 (3)	2.02 (3)	2.793 (4)	172 (5)

Symmetry codes: (iii) $1 - x, -y, 1 - z$; (v) $1 + x, y, z$; (vi) $1 - x, 1 - y, -z$; (vii) $x, 1 + y, z$.

The H atoms were located in a difference Fourier map. The O—H distance was constrained to be approximately the same for all H atoms. All other parameters, including U_{iso} values, were refined freely.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ATOMS* (Dowty, 1999); software used to prepare material for

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publication: *SHELXL*97 (Sheldrick, 1997) and *PLATON* (Spek, 1990).

References

Alaoui, A. T., Ouarsal, R., Lachkar, M., El Bali, B. & Bolte, M. (2002). *Acta Cryst.* E**58**, i91–i92.

Alaoui, A. T., Ouarsal, R., Lachkar, M., Zavalij, P. Y. & El Bali, B. (2003*a*). *Acta Cryst.* E**59**, i50–i52.

Alaoui, A. T., Ouarsal, R., Lachkar, M., Zavalij, P. Y. & El Bali, B. (2003*b*). *Acta Cryst.* E**59**, i68–i69.

Bruker (1999). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.

Dowty, E. (1999). *ATOMS for Windows and Macintosh*. Version 5. Shape Software, 521 Hidden Valley Road, Kingsport, TN 37663, USA.

El Bali, B., Boukhari, A., Aride, J. & Abraham, F. (1993). *J. Solid State Chem.* **104**, 453–459.

Lukaszewicz, K. (1967). *Bull. Acad. Pol. Sci. Ser. Sci. Chim.* **15**, 47–51.

Nord, A. G. (1983). *Acta Chem. Scand.* **37**, 539–543.

Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.

Sheldrick, G. M. (1997). *SHELXL*97 and *SHELXS*97. University of Göttingen, Germany.

Spek, A. L. (1990). *Acta Cryst.* A**46**, C-34.

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