Synthesis and Crystal Structure of Dysprosium Diphosphate $\text{KDyP}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$

A. Tahiri ALAOUL,* B. EL BALI,*† M. LACHKAR,** and R. GLAUM***

*Laboratory of Mineral Solid and Analytical Chemistry "LMSAC" Department of Chemistry, Faculty of Sciences, University Mohamed I, Po. Box 717, 60000 Oujda, Morocco

**Laboratoire d'Ingénierie des Matériaux Organométalliques et Moléculaires "L.I.M.O.M" Département de Chimie, Faculté des Sciences, BP 1796 Atlas, 30000 Fès, Morocco

***Institut für Anorganische Chemie, Universität Bonn, Gerhard-Domagk-Str. 1, D-53121 Bonn, Germany

A new mixed potassium dysprosium diphosphate, $\text{KDyP}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$, has been prepared *via* a soft chemistry route. It crystallizes in monoclinic, $P2_1/c$, cell dimensions: $a = 7.7133(7)\text{Å}$, $b = 10.5873(3)\text{Å}$, $c = 10.0548(3)\text{Å}$, $\beta = 93.28(9)^\circ$ and $Z = 4$. The 3D open framework is built from $[\text{DyO}_7]$ polyhedra sharing corners with $[\text{P}_2\text{O}_7]$ groups. The structure exhibit open channels running through the monoclinic cell along two directions $[100]$ and $[001]$, in which the water molecules and the K^+ ions are located.

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Rare earth diphosphates have attracted much attention, due mainly to their optical properties [refs. 1,2 and references therein]. They are especially suitable as host lattice for luminescent materials including laser devices [ref. 3 and references therein]. Within lanthanides elements, dysprosium is known to be a good dopant and activator for different inorganic lattices.

As a continuation of these investigations of lanthanides diphosphates,⁴ we hereby report on the synthesis and crystal structure of $\text{KDyP}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$.

Aqueous solutions of $\text{DyCl}_3 \cdot 6\text{H}_2\text{O}$ (1.5 mmol, 0.565 g) and $\text{K}_4\text{P}_2\text{O}_7$ (1.5 mmol, 0.495 g) were mixed with a few ml of dilute HCl. The mixture was stirred for 1 day. Then the evaporation of solvent water was allowed for around two weeks at room temperature. Prismatic colorless crystals were deposited, with the chemical composition determined after structure refinements (Fig. 1). They were filtered off and washed with a water-ethanol mixture (20:80).

A selected colorless crystal was collected at 293 K, using a CAD-4, Enraf-Nonius 4-circles diffractometer. Data were corrected for Lorentz and polarisation effects. The structure was refined using SHELXL-97 (Sheldrick, 1997).⁵ Starting atomic coordinates were taken from isotypic $\text{KTbP}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$.⁴ The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were found in successive difference-Fourier maps and refined isotropically.

Fig. 1 Chemical structure of the title compound.

† To whom correspondence should be addressed.
E-mail: belbali@fso.ump.ma

Crystal data and information on the refinement are summarized in Table 1. The final fractional atomic coordinates and isotropic displacement parameters are given in Table 2. CIF data from $\text{KDyP}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ have been deposited with FIZ (CSD-419427). Molecular graphics were created by using DIAMOND program.⁶

The 3D framework of the title compound results from vertices sharing $[\text{DyO}_7]$ polyhedra with chelating $[\text{P}_2\text{O}_7]$ diphosphate groups. The Dy, K and P coordination in the structure of the title compound, with the atomic numbering scheme, is depicted in Fig. 2. The structure is also characterized by the formation of open channels running through the monoclinic cell in two directions, $[100]$ and $[001]$, in which the water molecules and K^+ ions are located. Figure 3 shows a projection of the $\text{KDyP}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ structure down the slightly inclined c -axis, respectively. In addition, the Dy^{3+} cation is coordinated by two more diphosphate groups and one water molecule. The resulting polyhedron (Table 3) is a distorted pentagonal bipyramid with $d(\text{Dy}-\text{O})$ ranging from $2.234(7)\text{Å}$ up to $2.457(8)\text{Å}$. The average $d_{av}(\text{Dy}-\text{O})$ bond length of 2.308 Å is of the same magnitude as a similar average found in the isostructural compounds

Table 1 Crystal data and structure refinement for $\text{KDyP}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$.

Chemical formula, M	$\text{KDyP}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$, 411.57 g/mol
Wavelength (Mo K_α , Å)	0.71073
Crystal system, space group, Z	monoclinic, $P2_1/c$, 4
Unit cell dimensions (Å, °)	$a = 7.7133(7)$ $b = 10.5873(3)$ $\beta = 93.282(9)$ $c = 10.0548(3)$ $V = 819.76\text{ Å}^3$
θ -range(°)	4.35 – 25.97
Limiting indices	$-9 \leq h \leq 9$, $-13 \leq k \leq 0$, $-12 \leq l \leq 12$.
Reflections collected/unique	3177/1591 [$R(\text{int}) = 0.0772$]
Data/restraints/parameters	1591/6/131
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0404$, $wR_2 = 0.1023$
CCDC

Fig. 2 Asymmetric unit of $\text{KDyP}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ open framework. Symmetry: i) $1-x, 2-y, -z$; ii) $x, 1.5-y, 0.5+z$; iii) $2-x, 2-y, -z$; iv) $x, 1.5-y, 0.5+z$; v) $-1+x, y, z$; vi) $-1+x, 1.5-y, 0.5+z$.

Table 2 Atomic coordinates and equivalent isotropic displacement parameters U_{iso} ($\text{\AA}^2$).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{iso}
Dy	0.74951(5)	0.88011(4)	0.17021(4)	0.0085(3)
K	0.2527(3)	0.7839(3)	0.1488(3)	0.0267(6)
P1	0.6017(3)	0.8938(3)	-0.1678(2)	0.0090(5)
P2	0.9656(3)	0.8528(3)	-0.1279(3)	0.0097(5)
O1	0.5742(8)	0.8554(8)	-0.0262(7)	0.0152(16)
O2	0.4981(8)	1.0085(7)	-0.2171(7)	0.0122(15)
O3	0.5825(8)	0.7850(7)	-0.2631(7)	0.0138(16)
O4	0.8001(8)	0.9445(7)	-0.1719(7)	0.0137(15)
O5	0.9407(9)	0.8117(8)	0.0131(7)	0.0201(18)
O6	1.1242(9)	0.9324(8)	-0.1411(8)	0.0193(17)
O7	0.9577(8)	0.7426(7)	-0.2224(7)	0.0145(15)
O8	0.3747(12)	0.6224(9)	-0.0570(11)	0.035(2)
O9	0.7865(12)	0.9428(11)	0.4048(9)	0.035(2)
H81	0.422(16)	0.695(6)	-0.050(13)	0.042
H82	0.312(17)	0.614(11)	0.009(10)	0.042
H91	0.740(18)	1.011(6)	0.430(12)	0.042
H92	0.78(2)	0.890(9)	0.468(9)	0.042

$\text{KLnP}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ (Ln = Gd (2.352 $\text{\AA}$), Tb (2.345 $\text{\AA}$) and Yb (2.281 $\text{\AA}$)⁴ and 2.308 $\text{\AA}$ in $\text{KErP}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$.⁷ The $[\text{DyO}_7]$ pentagonal bipyramids are isolated in the structure with a $d_{\text{Dy-Dy}}$

Fig. 3 Projection of $\text{KDyP}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ structure down the slightly inclined *c*-axis.

value of over 5 $\text{\AA}$.

$\text{P}_2\text{O}_7^{4-}$ anions (Table 4) display two long distances $d(\text{P-O}_{\text{bridging}}) \sim 1.61 \text{ \AA}$ and six short distances, $d(\text{P-O}_{\text{terminal}}) \sim 1.505 \text{ \AA}$. The average P-O distances of 1.538 $\text{\AA}$ match those found in many other phosphates. The diphosphate group adopts a bent and eclipsed conformation, stabilized by the chelate-type coordination to the lanthanide cation. This coordination mode is also the reason for the rather small bridging angles $\angle(\text{P,O,P}) = 121.2(5)^\circ$.

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