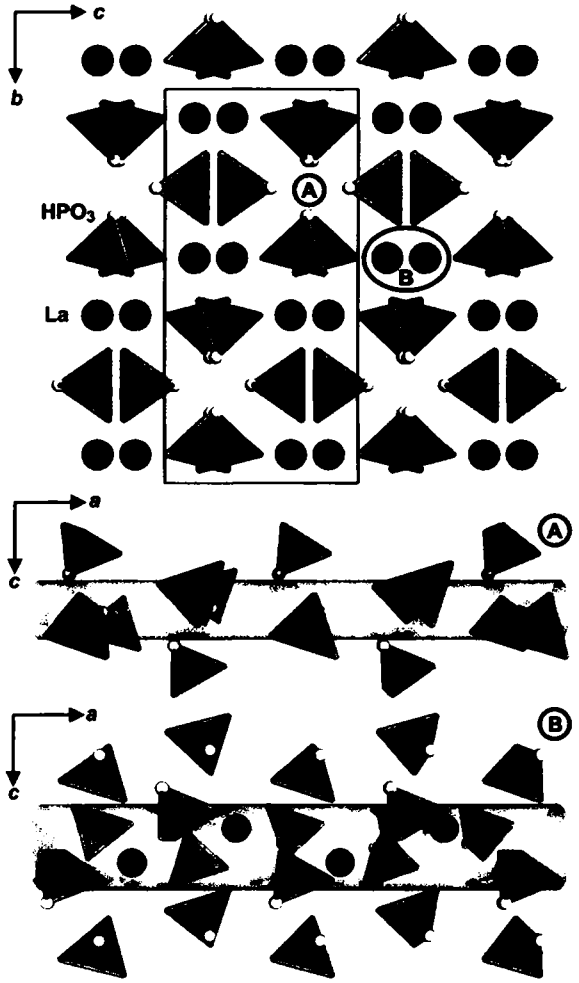
Crystal structure of dilanthanum tris(monohydrogenphosphate(III)), $La_2(HPO_3)_3$

B. Ewald, Yu. Prots and R. Kniep*

Max-Planck-Institut für Chemische Physik fester Stoffe, Nöthnitzer Str. 40, 01187 Dresden, Germany

Received October 19, 2005, accepted and available on-line December 5, 2005; CSD no. 409858



Abstract

$H_3La_2O_9P_3$, orthorhombic, *Pnma* (no. 62), $a = 8.305(2)$ Å, $b = 14.579(3)$ Å, $c = 7.059(1)$ Å, $V = 854.7$ Å^3, $Z = 4$, $R_{gt}(F) = 0.042$, $wR_{ref}(F^2) = 0.069$, $T = 295$ K.

Source of material

Crystals of the title compound were obtained by hydrothermal treatment of a mixture of lanthanum hydroxide, boron sesquioxide and sodium hypophosphite monohydrate in a Teflon autoclave ($V = 20$ ml) at 443 K. 0.750 g (3.949 mmol) $La(OH)_3$, 0.562 g (8.072 mmol) B_2O_3 and 1.712 g (16.152 mmol) $NaH_2PO_2 \cdot H_2O$ were intensively mixed by grinding in an agate mortar, transferred to the autoclave which was then filled with water up to a filling degree of 50 %. After a reaction duration of one week, the autoclave was removed from the furnace and allowed to cool down to room temperature. The raw product was separated from the mother liquor by vacuum filtration, washed with water and acetone, and finally dried at 333 K. X-ray powder diffraction reveals that $La_2(HPO_3)_3$ was not obtained as a single phased product. The sample contained $La(OH)_3$ and boric acid as crystalline impurities of which only the boric acid could be removed with an additional washing step. EDX analyses of isolated crystals comprise a ratio La : P = 0.71 which is in good agreement with the ratio of ⅔ obtained from the structure determination.

Discussion

Although rare earth phosphates(III) ("phosphites") have been investigated before [1-15], the crystal structure of $La_2(HPO_3)_3$ has not been reported so far. Focusing on the lanthanoid compounds, the crystal structures of some hydrated compounds with the general composition $Ln_2(HPO_3)_3 \cdot xH_2O$ (Ln = Nd, Pr [8], Eu [9]; x = 1, 2.5) have been reported. Furthermore some acid lanthanum and neodymium phosphites with varying degree of protonation and water content are known: $NdH(HPO_3)_2$ [10], $NdH(HPO_3)_2 \cdot H_2O$ [11], $La(H_2PO_3)_3 \cdot H_2O$ [12], $La(H_2PO_3)(HPO_3) \cdot 3H_2O$ [13], and $LaH(HPO_3)_2 \cdot 3H_2O$ [14]. The crystal structure of $Eu_2(HPO_3)_3$ [15] and $Sc_2(HPO_3)_3$ [6] represent the only examples of rare earth phosphites with the same formula like the title compound. While the scandium phosphite comprises a structural arrangement of high symmetry due to the octahedral coordination of Sc^{3+} ions [6], the europium compound with irregularly coordinated cations comprises structural similarities to the title compound but is not isotypic (monoclinic, space group *C2/m*).

The crystal structure of $La_2(HPO_3)_3$ contains two crystallographically independent distorted phosphite tetrahedra. These are considerably distorted due to differences in P—H (125(9) pm, 127(9) pm) and P—O (150.3(4) pm – 155.0(4) pm) distances and tetrahedral angles between 105(3)° and 118.4(3)° that clearly deviate from the ideal value. Size and shape of the phosphite groups are in good agreement with those found in related compounds. A view along the *a* axis (figure, top) shows that the complex anions are all pointing towards each other with the hydrogen corners. In this way hydrogen-lined channels parallel [100] are formed which are arranged layerwise along the *b* axis. Inbetween the phosphite channels corrugated layers of lanthanum cations are found. As the La^{3+} cations are beaded along the [100] in a staggered fashion, surrounded exclusively by the oxygen atoms of the phosphite groups, this arrangement can as well be described by a channel motif. Both types of channels are shown as a cut out in the bottom figure. Three adjacent phosphite tetrahedra form the aperture ($\varnothing \approx 230$ pm) of the hydrogen lined channels (A). Placed in oxygen lined channels (B), the crystallographically unique lanthanum is surrounded by seven phosphite groups and comprises irregular coordination by nine oxygen atoms.

* Correspondence author (e-mail: kniep@cpfs.mpg.de)

Table 1. Data collection and handling.

Crystal:	colorless platelet, size 0.010 × 0.040 × 0.080 mm
Wavelength:	Mo K_α radiation (0.7107 Å)
μ:	104.48 cm^{-1}
Diffractometer, scan mode:	Rigaku AFC-7, ω
$2\theta_{max}$:	64.92°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	7476, 1591
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1343
$N(param)_{refined}$:	74
Programs:	SHELXL-97 [16], DIAMOND [17]

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{iso}
HP(1)	8*d*	0.593(7)	0.679(4)	0.236(9)	0.01
HP(2)	4*c*	0.60(1)	¼	0.55(1)	0.02(2)

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
La(1)	8*d*	0.80167(3)	0.42730(2)	0.15246(4)	0.0074(1)	0.0120(1)	0.0077(1)	0.0004(1)	0.0000(1)	0.0018(1)
P(1)	8*d*	0.5495(2)	0.60276(8)	0.1642(2)	0.0093(5)	0.0084(5)	0.0071(6)	0.0000(4)	0.0001(5)	–0.0003(4)
P(2)	4*c*	0.5368(2)	¼	0.3877(3)	0.0095(8)	0.0090(7)	0.0119(9)	0	–0.0003(6)	0
O(1)	8*d*	0.5746(4)	0.3392(2)	0.2873(6)	0.013(2)	0.009(2)	0.022(2)	–0.002(1)	0.003(2)	0.004(1)
O(2)	8*d*	0.8748(5)	0.8885(3)	0.3882(6)	0.010(2)	0.033(2)	0.015(2)	–0.005(2)	0.005(2)	–0.005(2)
O(3)	8*d*	0.6622(4)	0.5725(3)	0.0061(5)	0.018(2)	0.016(2)	0.011(2)	0.009(2)	0.004(1)	0.003(1)
O(4)	8*d*	0.5667(4)	0.5323(2)	0.3274(5)	0.019(2)	0.013(2)	0.006(2)	–0.001(1)	–0.003(1)	0.002(1)
O(5)	4*c*	0.3570(6)	¼	0.4314(8)	0.012(2)	0.017(3)	0.021(3)	0	0.008(2)	0

Acknowledgment. Authors are thankful to Ms. K. Schulze for EDX analyses.

References

1. Petru, F.; Muck, A.: Über das Scandiumphosphit. Z. Anorg. Allg. Chem. **352** (1967) 330-332.
2. Kommissarova, L. N.; Melnicov, P. P.; Chernova, N. A.: On Scandium Phosphites. J. Less-Common Met. **13** (1967) 253-262.
3. Petru, F.; Muck, A.: Chromatographische Untersuchung von Produkten der Oxydation von Scandiumphosphit $Sc_2(HPO_3)_3$ durch Luftsauerstoff und von Produkten seiner thermischen Zersetzung im Vakuum. Z. Chem. **9** (1969) 38-39.
4. Petru, F.; Muck, A.: Beiträge zur Chemie der selteneren Elemente LXXVII. Coll. Czechoslov. Chem. Comm. **36** (1971) 3774-3779.
5. Ebert, M.; Kavan, L.: Scandium, Yttrium and Lanthanum Phosphites. J. Less-Common Met. **81** (1981) 55-60.
6. Ewald, B.; Prots, Yu.; Kniep, R.: Refinement of the crystal structure of di-scandium tris-monohydrogenphosphate(III), $Sc_2(HPO_3)_3$. Z. Kristallogr. NCS **218** (2003) 377-378.
7. Loub, J.: Crystal Chemistry of inorganic phosphites. Acta Crystallogr. **B47** (1991) 468-473.
8. Foulon, J.-D.; Tijani, N.; Durand, J.; Rafiq, M.; Cot, L.: Structure de $Ln_2(PO_3H)_3(H_2O)$ (*Ln* = Pr, Nd). Acta Crystallogr. C**49** (1993) i1-i4.
9. Foulon, J.-D.; Tijani, N.; Durand, J.; Rafiq, M.; Cot, L.: Structure de $Eu_2(PO_3H)_3 \cdot 2.5H_2O$. Acta Crystallogr. C**49** (1993) i849-i851.
10. Zakharova, B. S.; Ilyukhin, A. B.; Chudinova, N. N.: Synthesis and crystal structure of $NdH(PO_3H)_2$. Zh. Neorg. Khim. **48** (2003) 2004-2007.
11. Loukili, M.; Durand, J.; Larbot, A.; Cot, L.; Rafiq, M.: Structure de $NdH(PO_3H)_2 \cdot H_2O$. Acta Crystallogr. C**44** (1988) i6-i8.
12. Tijani, N.; Durand, J.; Cot, L.: Le phosphite acide de lanthane monohydrate. Acta Crystallogr. C**44** (1988) i2048-i2050.
13. Zhang, Y.; Hu, H.; Clearfield, A.: The crystal structures of two lanthanide phosphites and the geometry of metal phosphite complexes. Inorg. Chim. Acta **193** (1992) 35-42.
14. Loukili, M.; Durand, J.; Larbot, A.; Cot, L.; Rafiq, M.: Structure de $LaH(PO_3H)_2 \cdot 3H_2O$. Acta Crystallogr. C**47** (1991) i477-i479.
15. Foulon, J.-D.; Durand, J.; Cot, L.: $Eu_2(PO_3H)_3$. Acta Crystallogr. C**51** (1995) i348-i350.
16. Sheldrick, G. M.: SHELXL-97. Program for the Refinement of Crystal Structures. University of Göttingen, Germany 1997.
17. Brandenburg, K.: DIAMOND. Visual Crystal Structure Information System. Version 2.0f. Crystal Impact, Bonn, Germany 1998.