Mullica, D. F. & Sappenfield, E. L. (1991). *Acta Cryst.* C**47**, 2433–2435.
Mullica, D. F., Sappenfield, E. L. & Cunningham, T. A. (1991). *J. Solid State Chem.* **91**, 98–104.
Mullica, D. F., Sappenfield, E. L. & Perkins, H. O. (1988). *J. Solid State Chem.* **73**, 65–70.
Mullica, D. F., Sappenfield, E. L. & Perkins, H. O. (1989). *J. Solid State Chem.* **78**, 301–306.
Prandtl, W. & Mohr, S. (1938). *Z. Anorg. Allg. Chem.* **236**, 243–251.
Robinson, F. W. (1909). *J. Chem. Soc.* **95**, 1353–1359.
Sheldrick, G. M. (1989). *SHELXTL-Plus*. PC version. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Siemens (1994). *XP. Molecular Graphics Program*. Version 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Acta Cryst. (1996). C**52**, 2959-2960

Chlorapatite: $Ca_5(AsO_4)_3Cl$

Tina A. Wardojo[a] and Shiou-Jyh Hwu[b]

[a]*Department of Chemistry, Rice University, PO Box 1892, Houston, TX 77251, USA, and* [b]*Department of Chemistry, Clemson University, Clemson, SC 29634, USA. E-mail: shwu@clemson.edu*

(*Received 26 April 1995; accepted 9 September 1996*)

Abstract

Chlorapatite (pentacalcium triarsenate chloride), $Ca_5(AsO_4)_3Cl$ crystallizes in the hexagonal system and is closely related to its phosphate analogs, $Ca_5(PO_4)_3X$ (X = Cl, OH), but has a slightly modified structure in terms of anion sites.

Comment

The structure and chemistry of the apatites have been widely studied for many years due to their versatility in applications (Prener, 1967; Kreidler & Hummel, 1970; Elliott, 1994). The apatite structure [general formula $A_5(BO_4)_3X$, where A is a 2+ cation, B = P, As, V, Si or S, and X = F, Cl, Br, OH or CO_3] is adopted by a wide range of compounds.

The title compound adopts virtually the same structural framework as both $Ca_5(PO_4)_3Cl$ (Mackie, Elliott & Young, 1972) and $Ca_5(PO_4)_3OH$ (Kay, Young & Posner, 1964), with a slight variation due to the ordering of anions. The Cl atoms, which are disordered and have half occupancy, are located at (0,0,0.1263) and are symmetrical with respect to the mirror planes at $z = \frac{1}{4}$ and $z = \frac{3}{4}$. No single-crystal study of $Ca_5(AsO_4)_3Cl$ has been reported previously.

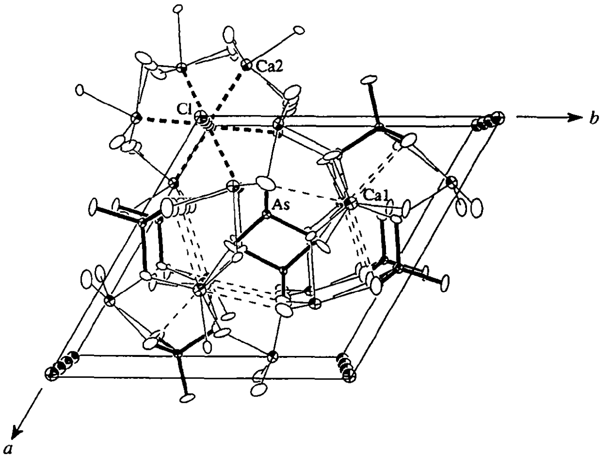

Fig. 1. Projection onto the (001) plane of the structure of $Ca_5(AsO_4)_3Cl$ showing the connectivity of the $Ca1O_9$, $Ca2O_5Cl$ and AsO_4 coordination geometries. Open circles represent O atoms. The Ca2—Cl bonds in $Ca2O_5Cl$ and the long Ca1—O bonds of the tricapped trigonal prism (viewed down its vertical axis) are drawn in thick and thin dotted lines, respectively. The atoms which were refined anisotropically are shown with ellipsoids at the 90% probability level.

Experimental

Crystals of the title compound were grown *via* an eutectic flux of 31% $CaCl_2$ and 69% NaCl (m.p. 773 K) from a reaction mixture of As_2O_5, CuO and Cu_2O (nominal composition $As_2Cu_4O_8$) in a fused-silica ampoule. The reactants were heated at 973 K for 6 d before being slowly cooled to room temperature. Apatite crystals were isolated by washing the reaction product with deionized water using suction filtration.

Crystal data

$Ca_5(AsO_4)_3Cl$
$M_r = 652.61$
Hexagonal
$P6_3/m$
$a = 10.076\,(1)$ Å
$c = 6.807\,(1)$ Å
$V = 598.4\,(2)$ Å^3
$Z = 2$
$D_x = 3.621$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 10–24°$
$\mu = 10.753$ mm^{-1}
$T = 296\,(2)$ K
Chunk
0.3 × 0.2 × 0.2 mm
Colorless

Data collection

Rigaku AFC-5*S* four-circle diffractometer
ω scans
1142 measured reflections
496 independent reflections
$R_{\rm int} = 0.0193$
$\theta_{\rm max} = 27.49°$

$h = -11 \rightarrow 11$
$k = -11 \rightarrow 11$
$l = -8 \rightarrow 8$
3 standard reflections monitored every 150 reflections
intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.0207$
$wR(F^2) = 0.0503$

Extinction correction: *SHELXL93* (Sheldrick, 1993)

$S = 1.169$
496 reflections
41 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0181P)^2 + 0.3376P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.885$ e Å^{-3}
$\Delta\rho_{\min} = -0.627$ e Å^{-3}

Extinction coefficient: 0.0141 (10)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
As1	0.40949 (5)	0.03079 (5)	1/4	0.0068 (2)
Ca1	1/3	2/3	0.0050 (2)	0.0111 (2)
Ca2	0.26988 (10)	0.24976 (10)	1/4	0.0105 (2)
Cl1†	0	0	0.1263 (5)	0.0218 (6)
O1	0.1559 (4)	0.5081 (4)	0.2500	0.0144 (7)
O2	0.5347 (4)	0.3966 (3)	0.2500	0.0116 (6)
O3	0.3511 (3)	0.0892 (3)	0.0535 (4)	0.0174 (5)

† Site occupancy = 0.5.

Table 2. *Selected geometric parameters (Å, °)*

As1—O1$^{\rm i}$	1.669 (3)	Ca1—O3$^{\rm vi}$	2.915 (2)
As1—O3$^{\rm ii}$	1.681 (2)	Ca1—O3$^{\rm viii}$	2.915 (2)
As1—O3	1.681 (2)	Ca1—O3$^{\rm vii}$	2.915 (2)
As1—O2$^{\rm iii}$	1.696 (3)	Ca2—O2	2.316 (3)
Ca1—O1$^{\rm iv}$	2.382 (2)	Ca2—O3$^{\rm ix}$	2.324 (2)
Ca1—O1	2.382 (2)	Ca2—O3$^{\rm vii}$	2.324 (2)
Ca1—O1$^{\rm v}$	2.382 (2)	Ca2—O3	2.530 (2)
Ca1—O2$^{\rm vi}$	2.456 (2)	Ca2—O3$^{\rm ii}$	2.530 (2)
Ca1—O2$^{\rm vii}$	2.456 (2)	Ca2—Cl1	2.7557 (14)
Ca1—O2$^{\rm viii}$	2.456 (2)	Ca2—Cl1$^{\rm ii}$	2.7557 (14)

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

The intensities were corrected for the anisotropic part of the absorption using a ψ scan, however, for logistical reasons, it was impossible to apply the spherical absorption correction subsequently requested by the editor.

Data collection: *TEXSAN* (Molecular Structure Corporation, 1989). Cell refinement: *TEXSAN*. Data reduction: *TEXSAN*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1991). Software used to prepare material for publication: Microsoft *WORD*5.1a.

Financial support for this research (DMR-9208529) and the single-crystal X-ray diffractometer from the National Science Foundation is gratefully acknowledged.

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: BR1116). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Elliott, J. C. (1994). In *Structure and Chemistry of the Apatites and Other Calcium Orthophosphates*. Amsterdam: Elsevier.
Kay, I. M., Young, R. A. & Posner, A. S. (1964). *Nature*, **204**, 1050–1052.
Kreidler, E. R. & Hummel, F. A. (1970). *Am. Mineral.* **55**, 170–184.
Mackie, P. E., Elliott, J. C. & Young, R. A. (1972). *Acta Cryst.* B**28**, 1840–1848.
Molecular Structure Corporation (1989). *TEXSAN. Single Crystal Structure Analysis Software*. Version 5.0. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Prener, J. S. (1967). *J. Electrochem. Soc.* **114**, 77–83.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1991). *SHELXTL-Plus*. Release 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Acta Cryst. (1996). C**52**, 2960-2963

A Mixed Nickel–Lithium Pyrophosphate, $LiNi_{1.5}P_2O_7$

K. Rissouli,[a] K. Benkhouja,[a] A. Sadel,[a]
M. Bettach,[a] M. Zahir,[a] M. Giorgi[b] and M. Pierrot[b]

[a]*Laboratoire de Physico-chimie des Matériaux, Département de Chimie, Faculté des Sciences, Université Chouaib Doukkali, BP 20 El Jadida, Morocco, and* [b]*LBS-URA 1409, Centre Scientifique Saint Jérôme, 13397 Marseille, France*

(*Received 27 November 1995; accepted 26 February 1996*)

Abstract

The title compound, dilithium trinickel bis(diphosphate), is composed of $[P_2O_7]$ layers parallel to the crystallographic plane (001), separated by chains of $[NiO_6]$ octahedra. The coordination polyhedra of the Li^+ ions link the $[P_2O_7]$ groups and the $[NiO_6]$ octahedra, and so ensure the cohesion of the structure.

Comment

Work on mixed pyrophosphates ABP_2O_7 has shown that the structural type of these compounds depends upon the size of the *A* and *B* cations and the conformation of the $[P_2O_7]$ groups. With two cations of different size, particularly an alkaline earth cation and a transition metal cation, mixed pyrophosphates crystallize in one of three types of structure: cage (Riou, Labbe & Goreaud, 1988*b*), sheet (Riou, Labbe & Goreaud, 1988*a*; Moqine, Boukhari & Holt, 1991; Alaoui El Belghiti, Boukhari & Holt, 1991; Riou, Leligny, Pham, Labbe & Raveau, 1991) or tunnel (Riou & Goreaud, 1990; Murashova, Velikodnyi & Trunov, 1991; Riou & Raveau, 1991). When two different 3*d* transition elements are present, the structure is composed of a succession of metal planes separated by layers of $[P_2O_7]$ groups. The conformation of the P_2O_7 groups is staggered and the

Acta Crystallographica Section C
ISSN 0108-2701 © 1996