

The triple pyrophosphate $\text{Cs}_3\text{CaFe}(\text{P}_2\text{O}_7)_2$

Nataliya Yu. Strutynska,^a Vyacheslav N. Baumer,^b Igor V. Zatovsky,^{a*} Artem A. Babaryk^a and Nikolay S. Slobodyanik^a

^aDepartment of Inorganic Chemistry, Taras Shevchenko National University, 64, Volodymyrska Street, 01033 Kyiv, Ukraine, and ^bSTC 'Institute for Single Crystals', NAS of Ukraine, 60 Lenin Avenue, 61001 Kharkiv, Ukraine
Correspondence e-mail: zvigov@yandex.ru

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The complex phosphate tricaesium calcium iron bis(diphosphate), $\text{Cs}_3\text{CaFe}(\text{P}_2\text{O}_7)_2$, has been prepared by the flux method. Isolated $[\text{FeO}_5]$ and $[\text{CaO}_6]$ polyhedra are linked by two types of P_2O_7 groups into a three-dimensional framework. The latter is penetrated by hexagonal channels along the a axis where three Cs atoms are located. Calculations of caesium Voronoi–Dirichlet polyhedra give coordination schemes for the three Cs atoms as $[8 + 3]$, $[9 + 1]$ and $[9 + 4]$. The structure includes features of both two- and three-dimensional frameworks of caesium double pyrophosphates.

Comment

Double pyrophosphates of caesium and polyvalent metals have been widely investigated, for instance, $\text{Cs}_2M^{\text{II}}\text{P}_2\text{O}_7$ ($M^{\text{II}} = \text{Ca}$ or Sr ; Zatoovsky *et al.*, 2008; Trunov *et al.*, 1991) and $\text{Cs}M^{\text{III}}\text{P}_2\text{O}_7$ ($M^{\text{III}} = \text{V}$, Cr , Fe , Mo or Yb ; Wang & Lii, 1989; Linde & Gorbunova, 1982; Millet & Mentzen, 1991; Lii & Haushalter, 1987; Jansen *et al.*, 1991), as well as a set of oxyphosphates, *viz.* $\text{Cs}_2M^{\text{IV}}\text{OP}_2\text{O}_7$ ($M^{\text{IV}} = \text{Ti}$ or V ; Protas *et al.*, 1991; Lii & Wang, 1989), $\text{Cs}M^{\text{V}}\text{OP}_2\text{O}_7$ ($M^{\text{V}} = \text{Nb}$ or Mo ; Nikolaev *et al.*, 1982; Guesdon *et al.*, 1994) and $\text{CsUO}_2\text{P}_2\text{O}_7$ (Linde *et al.*, 1981). However, there are no examples of compounds containing caesium with different polyvalent metals. We report herein the structure of a new triple pyrophosphate, $\text{Cs}_3\text{CaFe}(\text{P}_2\text{O}_7)_2$, (I), prepared from a self-flux synthesis.

The structure of (I) is built up from isolated $[\text{CaO}_6]$ and $[\text{FeO}_5]$ polyhedra interlinked *via* two types of P_2O_7 groups (Fig. 1). Fe atoms form two types of six-membered rings $[\text{Fe}(\text{OP})_2\text{O}]$ due to the chelating role of pyrophosphate. The values of these four Fe–O distances lie in the range of 1.912 (5)–1.993 (5) Å. Completeness of the $[\text{FeO}_5]$ polyhedra is achieved by an additional monodentate P_2O_7 group attached above the ring with a slightly shortened Fe–O

distance of 1.882 (5) Å. The Ca atoms are in a quite distorted octahedron composed of one bidentate and four monodentate pyrophosphates. As a result, the main $[\text{CaFe}(\text{P}_2\text{O}_7)_2]$ structural unit is formed giving an anionic three-dimensional framework. The latter is penetrated by hexagonal channels along the direction $[100]$, where three types of Cs atoms are located (Fig. 2).

Caesium polyhedra in double pyrophosphates are generally described with the cut-off Cs–O distance up to 3.6 Å. Taking into account this assumption for (I), the oxygen coordination of caesium can be exemplified as Cs_1O_{10} , Cs_2O_8 and Cs_3O_6 ; in this crystal they are represented by open polyhedra. For a more precise determination of the coordination numbers (CN) of Cs1–Cs3, Voronoi–Dirichlet polyhedra (VDP) were constructed using the *DIRICHLET* program included in the *TOPOS* package (Blatov *et al.*, 1995). The general considerations concerning the VDP calculations were applied as previously described (Blatov *et al.*, 1998). All details connected with this procedure are given as supplementary materials and will not be discussed here. Analysis of the solid angle (Ω) distribution for each case revealed 11 Cs–O contacts of Cs1 and Cs2 up to 4.1 Å [$R(\text{Cs1–O})_{\text{av}} = 3.876$ Å and $R(\text{Cs2–O})_{\text{av}} = 3.671$ Å], neglecting those corresponding to $\Omega < 1.5\%$ (Blatov *et al.*, 1998). Thus, the coordination scheme for Cs1 and Cs2 is described as $[8 + 3]$ and $[9 + 1]$: eight/nine contacts are in the range 2.978 (4)–3.574 (5) Å meaning 'ion-covalent' bonds. The three/one are in the range 3.579 (5)–3.964 (5) Å corresponding to $1.5\% < \Omega < 5\%$ and it is noteworthy that the solid angle [$\Omega = 1.57\%$, $R(\text{Cs2–O14}) = 4.342$ Å] for the longest contact is in the vicinity of the cut-off value. The same considerations are correct for Cs3, resulting in a $[9 + 4]$ scheme at a cut-off distance of 4.113 Å.

The composition of (I) may be represented as $\text{Cs}_2\text{CaP}_2\text{O}_7 \times \text{CsFeP}_2\text{O}_7$. In comparison, the structure of $\text{Cs}_2\text{CaP}_2\text{O}_7$ (Zatoovsky *et al.*, 2008) also contains isolated $[\text{CaO}_6]$ octahedra in layers organized into a three-dimensional framework by the P_2O_7 unit. Caesium resides in hexagonal channels between the above-mentioned layers. The second structure, CsFeP_2O_7

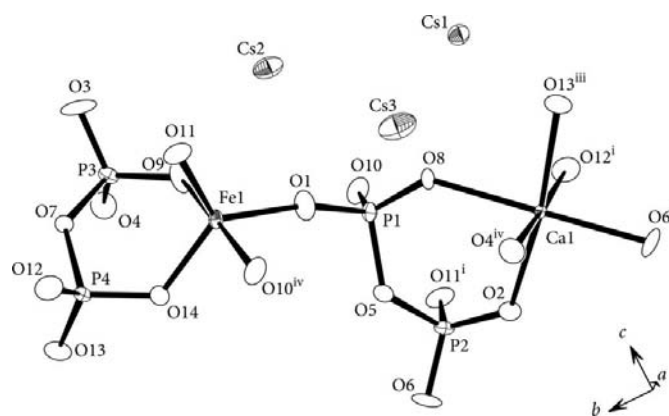


Figure 1

A connected set of numbered atoms in (I), showing displacement ellipsoids at the 50% probability level. [Symmetry codes: (i) $\frac{1}{2} + x, \frac{1}{2} - y, -z$; (ii) $1 - x, -\frac{1}{2} + y, -\frac{1}{2} - z$; (iii) $x, -1 + y, z$; (iv) $-\frac{1}{2} + x, \frac{1}{2} - y, -z$.]

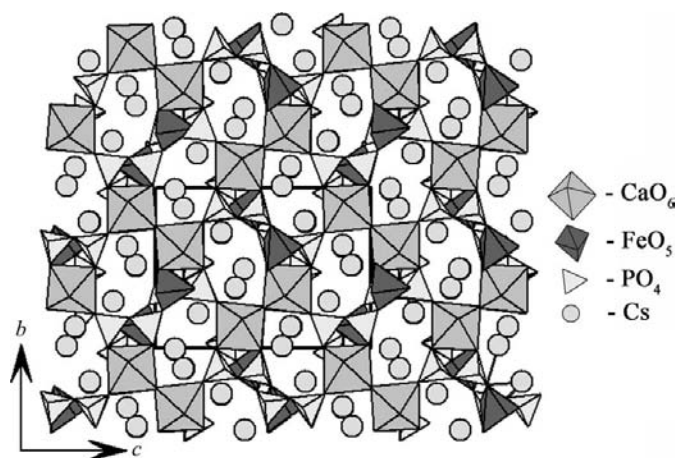


Figure 2
A projection of (I) on the *bc* plane.

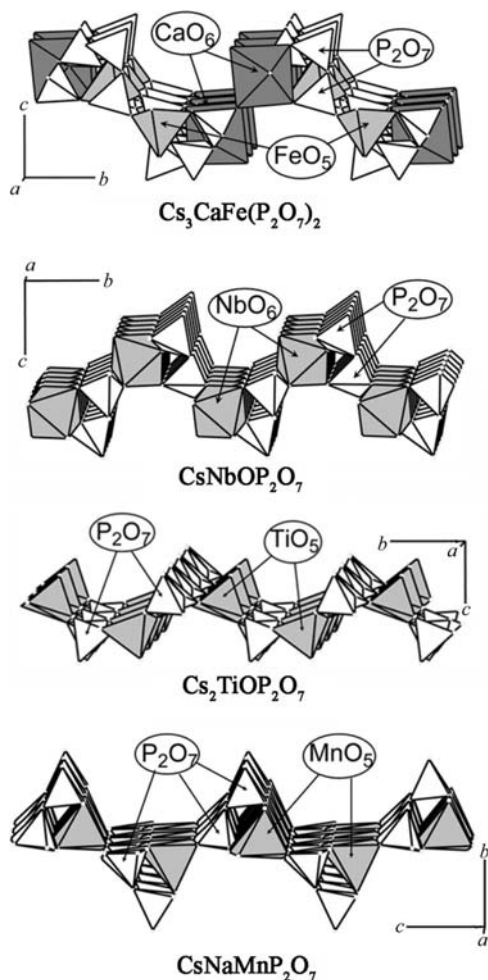


Figure 3
The formation of zigzag layers in complex pyrophosphates.

(Millet & Mentzen, 1991), differs significantly from (I) and is built up from isolated $[\text{FeO}_6]$ linked into pairs by pyrophosphate bridges into ribbons. Because of the alternation in a chessboard-like order into a three-dimensional net, the channels with Cs atoms appear.

In the case of (I), the anionic $[\text{CaFe}(\text{P}_2\text{O}_7)_2]^{3-}$ sublattice can be seen as containing zigzag layers (Fig. 3) attached to each other *via* one of the P_2O_7 groups. Aggregation of $[\text{MO}_n]$ ($n = 5$ or 6) with P_2O_7 into layers is common for a set of complex pyrophosphates, for example, $\text{CsNaMnP}_2\text{O}_7$ (Huang & Hwu, 1998), $\text{Cs}_2\text{TiOP}_2\text{O}_7$ (Protas *et al.*, 1991), $\text{Cs}_2\text{VOP}_2\text{O}_7$ (Lii & Wang, 1989), $\text{CsNbOP}_2\text{O}_7$ (Nikolaev *et al.*, 1982) and $\text{Cs}_2\text{UO}_2\text{P}_2\text{O}_7$ (Linde *et al.*, 1981). According to the structural data, these layers can be either flat or zigzag (Fig. 3) and are separated from each other by sheets of alkaline metals. Consequently, the structure of (I) contains features of both layered and three-dimensional frameworks simultaneously.

Experimental

The title triple pyrophosphate, (I), was obtained from a high-temperature solution in the system $\text{Cs}_2\text{O}-\text{P}_2\text{O}_5-\text{Fe}_2\text{O}_3-\text{CaO}$. H_3PO_4 (0.3 ml containing 0.392 g H_3PO_4) was added dropwise to a ground mixture of CsPO_3 (2.000 g), Fe_2O_3 (0.215 g) and CaCO_3 (0.268 g). The composition obtained, corresponding to a molar ratio $\text{Cs}/\text{P} = 0.7$, $\text{Fe}/\text{P} = 0.2$ and $\text{Ca}/\text{P} = 0.2$, was heated slowly in a platinum crucible up to a temperature of 1223 K and kept at this temperature for a period of 1 h. Crystallization at 1023 K was performed for a period of 5 h. The resulting melt contained colourless prismatic crystals of (I) which were leached out using deionized water to dissolve the superfluous flux.

Table 1
Selected geometric parameters (\AA , $^\circ$).

Ca1—O6 ⁱ	2.294 (5)	Cs2—O3	3.964 (5)
Ca1—O13 ⁱⁱ	2.310 (5)	Cs3—O3 ^v	3.127 (5)
Ca1—O4 ⁱⁱⁱ	2.339 (4)	Cs3—O2 ^{vii}	3.416 (5)
Ca1—O2	2.341 (5)	Cs3—O4 ⁱⁱⁱ	3.426 (5)
Ca1—O8	2.346 (5)	Cs3—O14 ⁱⁱⁱ	3.427 (5)
Ca1—O12 ^{iv}	2.379 (5)	Cs3—O12 ⁱⁱ	3.482 (5)
Fe1—O1	1.882 (5)	Cs3—O6 ^{vii}	3.678 (6)
Fe1—O11	1.914 (4)	Cs3—O9 ⁱⁱⁱ	3.723 (6)
Fe1—O14	1.923 (5)	Cs3—O13 ⁱⁱ	3.772 (6)
Fe1—O10 ⁱⁱⁱ	1.992 (5)	Cs3—O8	3.168 (5)
Fe1—O9	1.963 (5)	Cs3—O1	3.704 (6)
Cs1—O3 ^v	3.054 (5)	Cs3—O13 ⁱⁱⁱ	3.845 (5)
Cs1—O11 ^v	3.088 (4)	Cs3—O5 ⁱⁱⁱ	4.021 (5)
Cs1—O8	3.090 (5)	Cs3—O10 ⁱⁱⁱ	4.113 (5)
Cs1—O13 ⁱⁱ	3.100 (5)	P1—O8	1.491 (5)
Cs1—O7 ⁱⁱ	3.141 (5)	P1—O10	1.519 (5)
Cs1—O14 ^{iv}	3.215 (5)	P1—O1	1.522 (5)
Cs1—O4 ⁱⁱ	3.282 (5)	P1—O5	1.644 (5)
Cs1—O6 ^{vi}	3.359 (5)	P2—O6	1.487 (5)
Cs1—O13 ^{iv}	3.579 (5)	P2—O2	1.509 (5)
Cs1—O12 ^{iv}	3.588 (5)	P2—O11 ^{iv}	1.541 (4)
Cs1—O10	3.879 (5)	P2—O5	1.616 (5)
Cs2—O7 ^v	2.977 (4)	P3—O4	1.484 (5)
Cs2—O5 ^{iv}	3.020 (4)	P3—O3	1.488 (5)
Cs2—O10	3.045 (5)	P3—O9	1.535 (5)
Cs2—O9	3.094 (5)	P3—O7	1.646 (5)
Cs2—O12 ^v	3.182 (5)	P4—O13	1.495 (5)
Cs2—O6 ^{iv}	3.474 (5)	P4—O12	1.503 (5)
Cs2—O3 ^v	3.527 (6)	P4—O14	1.542 (5)
Cs2—O2 ^{vi}	3.571 (5)	P4—O7	1.635 (4)
Cs2—O1	3.699 (5)		
P2—O5—P1	124.7 (3)	P4—O7—P3	131.9 (3)

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

*Crystal data*Cs₃CaFe(P₂O₇)₂ $M_r = 842.54$ Orthorhombic, $P2_12_12_1$ $a = 9.3001$ (4) Å $b = 11.2399$ (5) Å $c = 15.1010$ (6) Å $V = 1578.54$ (12) Å³ $Z = 4$ Mo $K\alpha$ radiation $\mu = 8.57$ mm⁻¹ $T = 293$ K $0.1 \times 0.03 \times 0.01$ mm*Data collection*

Oxford Diffraction KM-4/Xcalibur diffractometer with a Sapphire3 detector

Absorption correction: multi-scan (Blessing, 1995)

 $T_{\min} = 0.481$, $T_{\max} = 0.919$

11400 measured reflections

4578 independent reflections

3632 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.062$ *Refinement* $R[F^2 > 2\sigma(F^2)] = 0.036$ $wR(F^2) = 0.069$ $S = 0.97$

4578 reflections

209 parameters

 $\Delta\rho_{\text{max}} = 1.24$ e Å⁻³ $\Delta\rho_{\text{min}} = -1.64$ e Å⁻³

Absolute structure: Flack (1983),

1966 Friedel pairs

Flack parameter: -0.01 (2)

Data collection: *CrysAlis Pro* (Oxford Diffraction, 2009); cell refinement: *CrysAlis Pro*; data reduction: *CrysAlis Pro*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 1999); 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: FN3046). Services for accessing these data are described at the back of the journal.

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