

Al2—O11	1.9562 (12)	Na6—O3 ^{iv}	2.3119 (13)
Al2—O10	1.9927 (13)	Na6—O6 ^{iv}	2.4031 (14)
Na1—O1	2.2896 (15)	Na6—O11	2.4074 (15)
Na1—O8 ⁱ	2.3673 (13)	Na6—O16 ^{iv}	2.488 (2)
Na1—O2	2.3687 (14)	Na6—O20	2.619 (2)
Na1—O12 ⁱ	2.4197 (14)	Na7—O7	2.2909 (13)
Na1—O19 ⁱ	2.461 (2)	Na7—O6 ^{iv}	2.3692 (14)
Na1—O12	2.6438 (13)	Na7—O21 ⁱⁱⁱ	2.3715 (15)
Na2—O2	2.3337 (13)	Na7—O15 ⁱⁱⁱ	2.413 (2)
Na2—O9	2.3421 (13)	Na7—O11	2.4479 (13)
Na2—O5	2.4110 (15)	Na7—O4 ^{iv}	2.5113 (14)
Na2—O19	2.459 (2)	Na8—O3 ^{iv}	2.3442 (14)
Na2—O12	2.4964 (14)	Na8—O4 ^{iv}	2.3918 (14)
Na2—O17	2.510 (2)	Na8—O3 ⁱⁱⁱ	2.3988 (13)
Na3—O1	2.3255 (13)	Na8—O5 ⁱⁱⁱ	2.4301 (13)
Na3—O12	2.3418 (14)	Na8—O17 ⁱⁱⁱ	2.464 (2)
Na3—O15 ⁱⁱ	2.365 (2)	Na8—O11	2.6012 (13)
Na3—O10	2.3663 (13)	Na9—O15 ^v	2.3648 (15)
Na3—O18 ⁱⁱ	2.440 (2)	Na9—O7 ^{iv}	2.3705 (14)
Na3—O5	2.4894 (13)	Na9—O10 ^{vi}	2.4002 (13)
Na4—O9	2.3559 (14)	Na9—O18	2.458 (2)
Na4—O11 ⁱⁱⁱ	2.3656 (14)	Na9—O20	2.525 (2)
Na4—O9 ⁱⁱⁱ	2.4126 (13)	Na9—O10 ⁱⁱⁱ	2.5767 (15)

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

Table 3. Hydrogen-bonding geometry ($\text{\AA}, ^\circ$)

D—H...A	D—H	H...A	D...A	D—H...A
O5—H5...O4	0.71 (2)	2.37 (2)	2.712 (2)	112 (2)
O6—H6...O1	0.74 (2)	2.39 (2)	2.723 (2)	109 (2)
O8—H8...O14	0.72 (2)	2.31 (2)	3.033 (2)	174 (3)
O16—H161...O13 ⁱ	0.77 (3)	2.29 (3)	3.062 (2)	176 (3)
O16—H162...O13	0.89 (3)	1.77 (3)	2.643 (2)	167 (2)
O17—H171...O13	0.71 (3)	2.27 (3)	2.982 (3)	179 (3)
O17—H172...O15	1.10 (4)	1.42 (4)	2.520 (2)	174 (3)
O18—H181...O14	0.78 (3)	1.79 (3)	2.562 (2)	171 (3)
O18—H182...O17	0.78 (3)	2.07 (3)	2.823 (2)	163 (3)
O19—H191...O18 ⁱⁱ	0.74 (3)	2.61 (3)	3.251 (3)	146 (3)
O19—H192...O14	0.91 (3)	1.75 (3)	2.652 (2)	170 (3)
O20—H201...O21	0.79 (2)	2.06 (3)	2.841 (2)	172 (2)
O20—H202...O14	0.80 (2)	1.84 (3)	2.632 (2)	170 (2)
O21—H211...O4 ⁱⁱⁱ	0.82 (2)	2.00 (2)	2.804 (2)	170 (2)
O21—H212...O13 ^{iv}	0.92 (3)	1.64 (3)	2.553 (2)	173 (3)

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

Several attempts at data collection were undertaken, as the intensities of the standard reflections showed that the crystals decayed rapidly. One crystal, however, showed no decay. The solution of the structure was not straightforward; many reflections with odd l showed a marked weakness. It was difficult to recognize structural moieties within the proposed solutions. All but one of the proposed solutions failed to refine to a reasonable R value by least-squares procedures and consecutive difference Fourier syntheses. After the true solution was established, several data sets collected on decaying crystals were refined to R values of between 4.4 and 9.6%, after proper correction for the decay. These refinements were performed independently of each other to check the functionality of the O atoms (*i.e.* hydroxyl ion or water molecule). All gave the same indications and all H atoms were found in all structures, some with less reliability. This serves as confirmation of the functionality of the O atoms and that this phase is the main product of the synthesis. More chemical details will be published elsewhere (Weinberger, Schneider, Zabel, Müller & Geßner, 1996).

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure:

SHELXL93 (Sheldrick, 1993); *Xtal3.2* (Hall & Stewart, 1992). Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *SHELXL93*.

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Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: JZ1084). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A New Synthetic Fluoride Phosphate of Mixed-Valence Iron: $\text{Cs}_8\text{Fe}_8^{3+}\text{Fe}_7^{2+}\text{F}_{10}(\text{PO}_4)_{12}$

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Abstract

The title compound, octacaesium pentadecairon decafluoride dodecaphosphate, was prepared by hydrothermal methods. The structure contains three types of Fe

polyhedra (octahedra, tetrahedra and five-vertex polyhedra) which share vertices to form two-dimensional 'branched' layers approximately parallel to the (120) plane. These layers are linked into a framework by PO₄ tetrahedra. The Cs atoms occupy holes in the mixed Fe/P framework.

Comment

This work was carried out as part of a systematic study of phosphates formed with amphoteric complexes, in which the amphoteric complex can act as the cationic part of the structure or as another species of anion besides the orthophosphate ions. Compounds with two kinds of anions are often of technological interest, exhibiting, for example, pyro- and ferroelectricity or ion conductivity. To the best of our knowledge only five crystal structures of phosphates of this kind have been investigated, namely Cs₃Fe₄(PO₄)₅, Cs₇Fe₇(PO₄)₈O₂ (Andrewes-Allen & Robinson, 1988), CsFe₂P₅O₁₆ (Klinkert & Jansen, 1988), CsNaFe₉(PO₄)₆F₂ (Yakubovich & Mel'nikov, 1990) and CsFeH₅(PO₄)₃ (Anisimova, Serafine & Hoppe, 1995).

Five of the nine crystallographically independent Fe atoms in the title compound are in octahedral environments consisting of four O and two F atoms. The two F atoms occupy *trans* positions around Fe1, Fe6, Fe7 and Fe8, and *cis* positions around Fe5. The Fe1 octahedron has $\bar{1}$ symmetry and deviates only marginally from a regular octahedron (Table 2). The distance Fe1—F4 [1.971 (4) Å] is similar to the shorter of the two Fe1—O distances [1.978 (4) and 1.990 (4), average 1.984 Å]. The variation of the cation-anion distances in the Fe octahedra in general positions is substantially larger (Table 2).

Two crystallographically independent Fe atoms, Fe2 and Fe9, have tetrahedral coordination geometry. The Fe2 tetrahedron has C₂ symmetry and is the more regular, with two Fe2—O distances of 2.038 (5) and two of 2.066 (4) Å (average 2.052 Å). The bond lengths around Fe9, which lies on a general position, vary from 2.004 (5) to 2.097 (4) Å (average 2.054 Å). The average bond lengths are the same for both Fe tetrahedra.

The coordination polyhedra around Fe3 and Fe4 are distorted tetragonal pyramids, each consisting of one apical F atom and four O atoms [Fe3—F 2.128 (7), Fe4—F 2.090 (4) Å]. The Fe3 pyramid has C₂ symmetry and is the less distorted [Fe3—O 1.982 (5) and 2.046 (4), average 2.014 Å; Fe4—O 1.941 (5)–2.075 (5), average 2.011 Å]. Both Fe3 and Fe4 are disordered over two positions 1.01 (2) (Fe3··Fe31) and 1.24 (1) Å (Fe4··Fe41) apart. The ratio of the site occupancies for the two positions is 8:1 in both polyhedra.

The six independent PO₄ tetrahedra are not linked to each other, hence the compound is an orthophosphate. However, the orthophosphate tetrahedra are significantly

distorted; the P—O distances vary from 1.500 (4) to 1.568 (4) Å with an average of 1.532 Å.

The large Cs ions occupy different polyhedra. Cs1 possesses 9 + 4 coordination with nine anions in an inner sphere at 2.922 (4)–3.315 (5) Å and four anions at 3.498 (4)–3.563 (5) Å (average 3.277 Å). Cs2 is surrounded by nine anions at 2.962 (5)–3.239 (5) Å and two fluoride ions at 3.566 (2) and 3.593 (5) Å (average 3.181 Å). The coordination sphere of Cs3 consists of eight anions at 2.999 (4)–3.341 (5) Å and five more distant anions at 3.420 (6)–3.578 (4) Å (average 3.336 Å). The space available to Cs4 is even larger (the smallest distance is 3.114 Å) resulting in disorder of the Cs ion over the three sites Cs4, Cs4a and Cs4b, with an average cation-anion distance of 3.412 Å.

The analysis of the interatomic distances and bond-valence calculations using Pauling's second rule (Pauling, 1968) allowed us to fix the valence state of the nine independent Fe atoms. The resulting formula is Cs₄Fe₃³⁺[6o]Fe₇²⁺[4t]Fe₂³⁺[5y]Fe_{0.5}²⁺[6o]F₅(PO₄)₆. According to this formula, the Fe²⁺ cations are in tetrahedra (Fe2 and Fe9) and in five-vertex polyhedra (Fe3 and Fe4). The Fe³⁺ ions Fe1, Fe5, Fe7 and Fe8 occupy octahedra. The larger Fe6 octahedra are statistically occupied by Fe²⁺ and Fe³⁺ cations each with 50% probability. Mixed-valence iron in octahedra is typical for the structures of pegmatite phosphates (Moore, 1973) and has been noted in the structures of synthetic alluaudite (Yakubovich, Egorov-Tismenko, Simonov & Belov, 1977), arrojadite (Yakubovich, Matvienko, Simonov & Mel'nikov, 1986) and lipscombite (Matvienko, Yakubovich, Simonov & Belov, 1981). The dark colours (black, dark green, dark brown) of these kinds of phosphate are related to the disorder of the Fe²⁺ and Fe³⁺ ions (Moore, 1973).

As shown in Fig. 1, the octahedra are linked by common fluoride-ion vertices to form chains running perpendicular to the *ab* plane. Two of the six chains are all *trans* connected and four have two *cis* connected

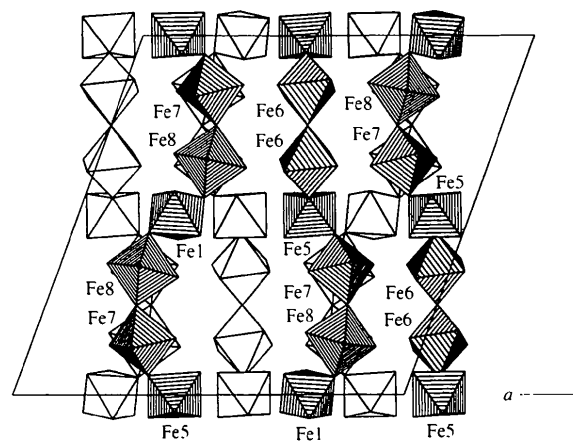


Fig. 1. Chains of Fe octahedra in the title compound in *ac* projection.

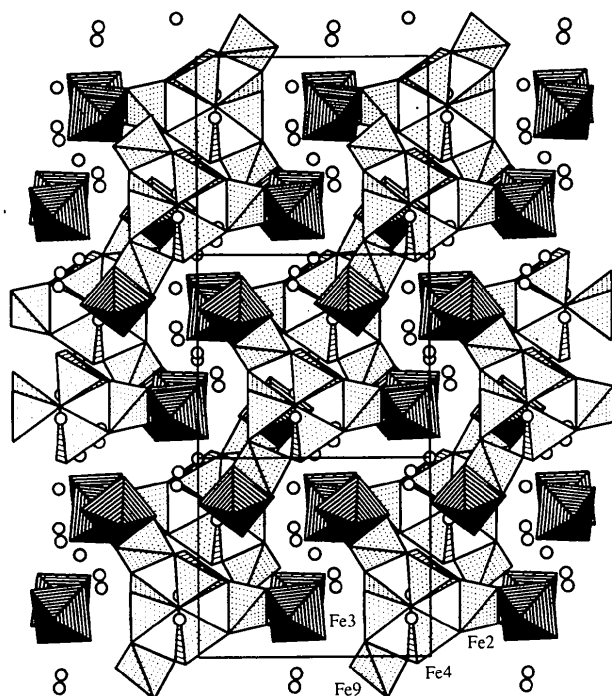


Fig. 2. Complex Fe polyhedral layers extending approximately parallel to the (120) plane. Fe octahedra are hatched, Fe tetrahedra and square pyramids are dotted, Cs atoms are shown as circles and PO_4 tetrahedra have been omitted.

octahedra. The direction of the chains results in pseudo orthorhombic symmetry with $a' = 19.450(4)$ Å. These chains are linked together in the a and b directions by groups of Fe^{2+} polyhedra. These groups are formed from three square pyramids with a common fluoride-ion corner (F2), which are further linked through three tetrahedra with common O-atom vertices (Fig. 2). To the best of our knowledge this kind of $\text{Fe}_6\text{O}_{18}\text{F}$ polyhedral group has not been found in a phosphate before.

The Fe2 and Fe9 tetrahedra in this group share two O-atom vertices (which do not interact with the Fe atoms in the pyramids) with the octahedra of the chains. Thus each group of six Fe^{2+} polyhedra links together three chains of octahedra to form thick layers of vertex-sharing Fe polyhedra (Fig. 2). The orientation of these layers is approximately parallel to the (120) plane. The layers of Fe polyhedra are further linked by PO_4 tetrahedra to give a three-dimensional $[\text{Fe}_{7.5}\text{F}_5(\text{PO}_4)_6]_{\infty\infty\infty}^{4-}$ framework.

As a result of the analysis of structure regularities in compounds containing mixed anions with amphoteric complexes, Sandomirskij & Belov (1984) have found that threefold connected polyhedra build 'loop' configurations inside the anionic network. In the present structure, all the O-atom vertices of the Fe polyhedra are shared with PO_4 tetrahedra, with just six of the 24 independent O atoms and one of the six F atoms being part

of three polyhedra. If we look at the interconnectivity of the polyhedra sharing one corner with two others, we find that they build a pattern with this loop configuration (Fig. 3). As the majority of the polyhedra share their vertices between two polyhedra only, the 'overcondensation' of the polyhedra is local. In this structure, the F and O atoms in these loops (F2, O8, O13, O14, O16, O18 and O24) are connected to the complex of six Fe^{2+} polyhedra. The bond valence of the O atoms is accounted for by large P—O distances towards these loop ligands (the largest distance in each independent orthophosphate tetrahedron corresponds to the P—O bond in the direction of the loop vertex). The disorder of Fe3 and Fe4 in the five-vertex polyhedra also results in a significant increase in the Fe31—F2 and Fe41—F2 distances and in a decrease of the bond valence towards the F2 ligand.

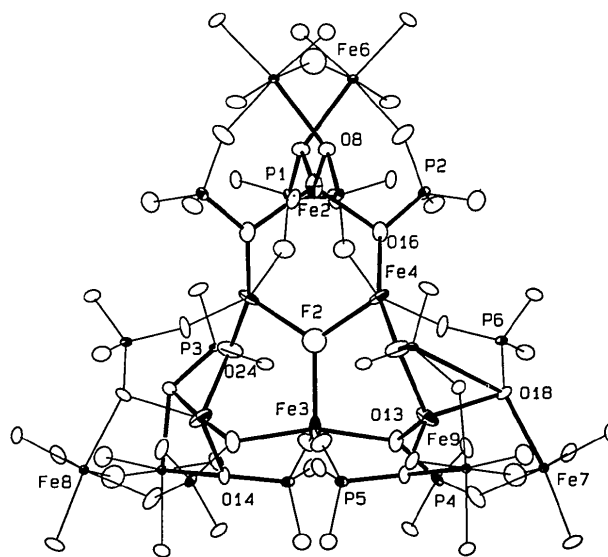


Fig. 3. Displacement ellipsoid plot (70% probability level) of the loop configuration. The bonds of triply connected anions are emphasized.

Experimental

Crystals of $\text{Cs}_8\text{Fe}_{15}\text{F}_{10}(\text{PO}_4)_{12}$ were grown in the system $\text{CsF}-\text{Fe}_2\text{O}_3-(\text{NH}_4)_2\text{HPO}_4-\text{H}_2\text{O}$ using hydrothermal techniques [$T = 673$ K, $P = 1000$ atm, 50% aqueous solution of CsF, $\text{Fe}_2\text{O}_3:(\text{NH}_4)_2\text{HPO}_4 = 1:2$ (1 atm = 101 325 Pa)]. Qualitative X-ray spectral analysis and chemical analysis showed the presence of Cs, Fe, P and F. As former studies of fluorophosphates had shown that OH groups are not found in crystals prepared at around this temperature and pressure, the chemical formula could be assigned on the basis of the crystal structure.

Crystal data

$\text{Cs}_8\text{Fe}_{15}\text{F}_{10}(\text{PO}_4)_{12}$
 $M_r = 3230.67$

Mo $K\alpha$ radiation
 $\lambda = 0.71073$ Å

Monoclinic

$C2/c$
 $a = 21.316 (11) \text{ \AA}$
 $b = 12.296 (7) \text{ \AA}$
 $c = 20.686 (8) \text{ \AA}$
 $\beta = 109.98 (6)^\circ$
 $V = 5095.5 (44) \text{ \AA}^3$
 $Z = 4$
 $D_x = 4.211 \text{ Mg m}^{-3}$

Cell parameters from 24

reflections
 $\theta = 10\text{--}13^\circ$
 $\mu = 10.298 \text{ mm}^{-1}$
 $T = 293 (2) \text{ K}$
 Sphere
 0.024 mm (radius)
 Dark brown

F4	0.1963 (2)	1.1780 (3)	0.0485 (2)	0.0129 (7)
F5	0.1728 (2)	0.6922 (3)	0.0533 (2)	0.0121 (7)
F6	0.2685 (2)	0.6490 (4)	0.2494 (2)	0.0230 (9)
O1	0.1362 (2)	0.6063 (4)	0.1567 (3)	0.0177 (10)
O2	0.3856 (2)	1.0200 (4)	0.1374 (2)	0.0143 (9)
O3	0.3946 (2)	0.5951 (4)	0.1739 (3)	0.0197 (10)
O4	0.5985 (2)	0.4425 (4)	0.1646 (2)	0.0144 (9)
O5	0.3004 (2)	0.7312 (4)	0.1378 (2)	0.0135 (9)
O6	0.4205 (2)	0.2149 (4)	0.1674 (2)	0.0173 (10)
O7	0.3292 (2)	1.1656 (4)	0.0572 (2)	0.0116 (8)
O8	0.0805 (2)	0.2908 (4)	0.3236 (2)	0.0109 (8)
O9	0.2268 (3)	0.3235 (4)	0.1569 (3)	0.0194 (10)
O10	0.1165 (2)	0.8911 (4)	0.0554 (2)	0.0114 (8)
O11	0.2017 (2)	1.0039 (4)	0.1403 (2)	0.0114 (8)
O12	0.0395 (2)	0.3195 (4)	0.1568 (2)	0.0173 (10)
O13	0.5572 (2)	0.2171 (4)	0.1896 (2)	0.0172 (10)
O14	0.1868 (2)	0.6504 (4)	0.3277 (2)	0.0105 (8)
O15	-0.0442 (2)	0.2968 (4)	-0.0642 (2)	0.0134 (9)
O16	0.5335 (2)	0.6283 (4)	0.1858 (2)	0.0178 (10)
O17	0.3669 (2)	0.6930 (4)	0.0632 (2)	0.0138 (9)
O18	0.3125 (2)	0.3116 (3)	0.3285 (2)	0.0099 (8)
O19	0.2229 (2)	1.1296 (4)	-0.0673 (2)	0.0122 (9)
O20	0.2578 (2)	0.9835 (4)	-0.1289 (3)	0.0168 (9)
O21	-0.0012 (2)	0.1813 (4)	0.0608 (2)	0.0147 (9)
O22	0.0178 (2)	0.5435 (4)	0.1224 (3)	0.0157 (9)
O23	0.1172 (2)	0.1885 (4)	0.1324 (3)	0.0194 (10)
O24	0.3402 (2)	0.3988 (4)	0.1942 (2)	0.0188 (10)

Data collection

Enraf-Nonius CAD-4
 diffractometer
 ω scans
 Absorption correction:
 ψ scans
 $T_{\min} = 0.66$, $T_{\max} = 0.96$
 6995 measured reflections
 6156 independent reflections
 5136 observed reflections
 $[I > 2\sigma(I)]$

$R_{\text{int}} = 0.0189$
 $\theta_{\text{max}} = 28^\circ$
 $h = -28 \rightarrow 27$
 $k = -16 \rightarrow 0$
 $l = -2 \rightarrow 27$
 3 standard reflections
 monitored every 250
 reflections
 intensity decay: 0.98%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.0357$
 $wR(F^2) = 0.0847$
 $S = 1.119$
 5917 reflections
 433 parameters
 $w = 1/[\sigma^2(F_o^2) + (0.0392P)^2 + 94.7503P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = -0.004$
 $\Delta\rho_{\text{max}} = 1.22 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -2.51 \text{ e \AA}^{-3}$

Extinction correction:
 SHELXL93 (Sheldrick,
 1993)

Extinction coefficient:
 0.000336 (13)

Atomic scattering factors
 from *International Tables*
 for *Crystallography* (1992),
 Vol. C, Tables 4.2.6.8 and
 6.1.1.4)

† Site occupancy 0.41 (2). ‡ Site occupancy 0.17 (3). § Site occupancy 0.42 (2). ¶ Site occupancy 0.896 (2). ** Site occupancy 0.104 (2).

Table 2. Selected geometric parameters (\AA , $^\circ$)

Fe1—F4 [†]	1.971 (4)	Fe6—F1 [‡]	2.018 (2)
Fe1—O19 [†]	1.978 (4)	Fe6—F3	2.026 (4)
Fe1—O7 [†]	1.990 (4)	Fe6—O12 [‡]	2.027 (5)
Fe2—O16 [‡]	2.038 (5)	Fe6—O8 [‡]	2.130 (4)
Fe2—O8	2.066 (4)	Fe7—O20 [†]	1.934 (5)
Fe3—O6 [‡]	1.982 (5)	Fe7—F5	1.953 (4)
Fe3—O13 [†]	2.046 (4)	Fe7—F6	1.957 (4)
Fe3—F2 [†]	2.128 (7)	Fe7—O5	1.967 (4)
Fe4—O3 [†]	1.941 (5)	Fe7—O1	2.002 (4)
Fe4—O4 [†]	1.956 (4)	Fe7—O18 [‡]	2.075 (4)
Fe4—O24 [‡]	2.074 (5)	Fe8—O23 [‡]	1.920 (5)
Fe4—O16 [†]	2.075 (5)	Fe8—O11	1.958 (5)
Fe4—F2 [†]	2.090 (4)	Fe8—F6 [‡]	2.000 (4)
Fe5—O21 [†]	1.943 (5)	Fe8—F4	2.007 (4)
Fe5—O10	1.960 (4)	Fe8—O9 [‡]	2.011 (5)
Fe5—O17 [†]	1.974 (4)	Fe8—O14 [†]	2.088 (4)
Fe5—O15 [†]	1.978 (4)	Fe9—O24	2.004 (5)
Fe5—F3 [†]	1.994 (4)	Fe9—O13 [†]	2.021 (5)
Fe5—F5	1.996 (4)	Fe9—O14 [†]	2.093 (5)
Fe6—O22 [‡]	1.987 (4)	Fe9—O18	2.097 (4)
Fe6—O2	1.991 (5)		

F4 [†] —Fe1—F4 [†]	180	O22 [‡] —Fe6—F3	88.3 (2)
F4 [†] —Fe1—O19 [†]	86.6 (2)	O2—Fe6—F3	91.3 (2)
F4 [†] —Fe1—O7 [†]	93.4 (2)	F1 [‡] —Fe6—F3	176.1 (2)
O19 [†] —Fe1—O19 [†]	180	O22 [‡] —Fe6—O12 [‡]	90.1 (2)
F4 [†] —Fe1—O7 [†]	90.8 (2)	O2—Fe6—O12 [‡]	173.2 (2)
F4 [†] —Fe1—O7 [†]	89.2 (2)	F1 [‡] —Fe6—O12 [‡]	93.2 (2)
O19 [†] —Fe1—O7 [†]	89.3 (2)	F3—Fe6—O12 [‡]	85.5 (2)
O19 [†] —Fe1—O7 [†]	90.7 (2)	O22 [‡] —Fe6—O8 [‡]	172.8 (2)
O7 [†] —Fe1—O7 [†]	180	O2—Fe6—O8 [‡]	91.4 (2)
O16 [‡] —Fe2—O16 [‡]	114.0 (3)	F1 [‡] —Fe6—O8 [‡]	85.6 (2)
O16 [‡] —Fe2—O8	109.0 (2)	F3—Fe6—O8 [‡]	90.6 (2)
O16 [‡] —Fe2—O8	98.2 (2)	O12 [‡] —Fe6—O8 [‡]	82.6 (2)
O8—Fe2—O8 [‡]	129.0 (3)	O20 [†] —Fe7—F5	91.2 (2)
O6 [‡] —Fe3—O6 [‡]	160.2 (3)	O20 [†] —Fe7—F6	95.0 (2)
Fe3 [†] —Fe3—O13 [†]	81.2 (2)	F5—Fe7—F6	173.8 (2)
O6 [‡] —Fe3—O13 [†]	89.4 (2)	O20 [†] —Fe7—O5	95.9 (2)
O6 [‡] —Fe3—O13 [†]	87.6 (2)	F5—Fe7—O5	88.2 (2)
O13 [†] —Fe3—O13 [†]	162.4 (3)	F6—Fe7—O5	91.4 (2)
O6 [‡] —Fe3—F2 [†]	99.89 (15)	O20 [†] —Fe7—O1	88.5 (2)
O13 [†] —Fe3—F2 [†]	98.8 (2)	F5—Fe7—O1	87.2 (2)
O3 [‡] —Fe4—O4 [†]	152.9 (2)	F6—Fe7—O1	92.8 (2)
O3 [‡] —Fe4—O24 [‡]	87.2 (2)	O5—Fe7—O1	173.7 (2)

Table 1. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

U_{iso} for Cs4, 4a and 4b, $U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$ for all others.

	x	y	z	$U_{\text{iso}}/U_{\text{eq}}$
Cs1	0.25811 (2)	0.92236 (3)	0.02653 (2)	0.01508 (10)
Cs2	0.16648 (2)	0.41782 (3)	0.25379 (2)	0.01613 (10)
Cs3	0.09046 (2)	0.40938 (4)	0.03250 (2)	0.01762 (10)
Cs4†	0.4380 (3)	0.4196 (3)	0.0740 (5)	0.0274 (3)
Cs4a‡	0.4466 (8)	0.4215 (5)	0.0819 (7)	0.0274 (3)
Cs4b§	0.4424 (2)	0.4164 (2)	0.0636 (3)	0.0274 (3)
Fe1	1/4	1/4	0	0.0047 (2)
Fe2	0	0.21852 (12)	1/4	0.0162 (3)
Fe3¶	0	0.74260 (15)	1/4	0.0153 (3)
Fe31**	0	0.6607 (13)	1/4	0.0153 (3)
Fe4¶	0.08399 (5)	0.99985 (9)	0.24660 (5)	0.0137 (2)
Fe41**	0.1335 (5)	1.0518 (7)	0.2466 (4)	0.0137 (2)
Fe5	0.08579 (4)	0.76056 (7)	-0.00086 (4)	0.0046 (2)
Fe6	0.46559 (4)	0.92817 (6)	0.14853 (4)	0.0046 (2)
Fe7	0.22197 (4)	0.66265 (7)	0.15022 (4)	0.0046 (2)
Fe8	0.21014 (4)	1.16218 (7)	0.14899 (4)	0.0047 (2)
Fe9	0.35010 (5)	0.26427 (9)	0.25145 (5)	0.0188 (2)
P1	0.36938 (7)	0.70117 (12)	0.13707 (7)	0.0053 (3)
P2	0.04758 (7)	0.20418 (12)	0.13304 (7)	0.0065 (3)
P3	0.27122 (7)	0.40319 (12)	0.13593 (7)	0.0071 (3)
P4	0.06288 (7)	0.64126 (12)	0.13198 (8)	0.0067 (3)
P5	0.36335 (7)	1.13769 (12)	0.13279 (7)	0.0062 (3)
P6	0.14998 (7)	0.91444 (12)	0.13209 (7)	0.0054 (3)
F1	0	0.4627 (6)	1/4	0.0271 (14)
F2	1/2	0.4156 (6)	1/4	0.0288 (14)
F3	0.4292 (2)	0.8833 (3)	0.0483 (2)	0.0139 (7)

O4 ^v —Fe4—O24 ^{iv}	88.5 (2)	O20 ⁱ —Fe7—O18 ^{iv}	172.3 (2)
O3 ^{iv} —Fe4—O16 ^v	88.7 (2)	F5—Fe7—O18 ^{iv}	87.1 (2)
O4 ^v —Fe4—O16 ^v	87.2 (2)	F6—Fe7—O18 ^{iv}	86.7 (2)
O24 ^{iv} —Fe4—O16 ^v	162.1 (2)	O5—Fe7—O18 ^{iv}	91.6 (2)
O3 ^{iv} —Fe4—F2 ^v	103.1 (2)	O1—Fe7—O18 ^{iv}	83.9 (2)
O4 ^v —Fe4—F2 ^v	104.0 (2)	O23 ^{viii} —Fe8—O11	95.5 (2)
O24 ^{iv} —Fe4—F2 ^v	100.8 (2)	O23 ^{viii} —Fe8—F6 ^{iv}	92.9 (2)
O16 ^v —Fe4—F2 ^v	97.2 (2)	O11—Fe8—F6 ^{iv}	89.8 (2)
O21 ^{vi} —Fe5—O10	97.3 (2)	O23 ^{viii} —Fe8—F4	91.2 (2)
O21 ^{vi} —Fe5—O17 ⁱ	92.6 (2)	O11—Fe8—F4	91.4 (2)
O10—Fe5—O17 ⁱ	90.5 (2)	F6 ^{iv} —Fe8—F4	175.5 (2)
O21 ^{vi} —Fe5—O15 ^{vi}	91.8 (2)	O23 ^{viii} —Fe8—O9 ^{viii}	89.5 (2)
O10—Fe5—O15 ^{vi}	91.4 (2)	O11—Fe8—O9 ^{viii}	174.9 (2)
O17 ⁱ —Fe5—O15 ^{vi}	174.9 (2)	F6 ^{iv} —Fe8—O9 ^{viii}	91.3 (2)
O21 ^{vi} —Fe5—F3 ⁱ	93.1 (2)	F4—Fe8—O9 ^{viii}	87.0 (2)
O10—Fe5—F3 ⁱ	169.6 (2)	O23 ^{viii} —Fe8—O14 ^{iv}	173.6 (2)
O17 ⁱ —Fe5—F3 ⁱ	88.1 (2)	O11—Fe8—O14 ^{iv}	90.5 (2)
O15 ^{vi} —Fe5—F3 ⁱ	89.2 (2)	F6 ^{iv} —Fe8—O14 ^{iv}	84.7 (2)
O21 ^{vi} —Fe5—F5	174.6 (2)	F4—Fe8—O14 ^{iv}	91.0 (2)
O10—Fe5—F5	87.4 (2)	O9 ^{viii} —Fe8—O14 ^{iv}	84.7 (2)
O17 ⁱ —Fe5—F5	84.5 (2)	O24—Fe9—O13 ^{ix}	118.5 (2)
O15 ^{vi} —Fe5—F5	90.9 (2)	O24—Fe9—O14 ^x	98.9 (2)
F3 ⁱ —Fe5—F5	82.2 (2)	O13 ^{ix} —Fe9—O14 ^x	108.0 (2)
O22 ^{vi} —Fe6—O2	95.7 (2)	O24—Fe9—O18	103.3 (2)
O22 ^{vi} —Fe6—F1 ^{vii}	95.4 (2)	O13 ^{ix} —Fe9—O18	99.8 (2)
O2—Fe6—F1 ^{vii}	89.6 (2)	O14 ^x —Fe9—O18	129.9 (2)

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

The metrically possible higher symmetry [rhombohedral cell, hexagonal setting: $a' = 12.296$, $b' = 12.304$, $c' = 58.323$ Å, $\alpha' = 89.91$, $\beta' = 90.00$, $\gamma' = 119.98^\circ$, transformation matrix $(-0.5 \ 0.5 \ 0 \ 0 \ -1 \ 0 \ 0 \ 1 \ 0 \ 3)$] was rejected because of the missing symmetry of the reflections (the R value for averaging reflections in the space group $R3$ was 0.33). The residual electronic density of 1.22 e \AA^{-3} is due to the disorder of the Cs4 atom, which was split over three sites and refined with one common isotropic displacement factor. The disordered Fe3 and Fe4 atoms were refined with a common anisotropic displacement factor.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994). Cell refinement: *CAD-4 EXPRESS*. Data reduction: *XCAD4* (Harms, 1992). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *TROMPLEU* (Gravereau, Larroche & leLirzin, 1991) and *ZORTEP* (Zsolnai, 1994). Software used to prepare material for publication: *SHELXL93*.

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Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: JZ1087). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Triaquahexathiocyanatobismuthlanthanum Dihydrate, $[\text{Bi}(\text{SCN})_6\text{La}(\text{H}_2\text{O})_3] \cdot 2\text{H}_2\text{O}$, and Triaquahexathiocyanatobismuthneodymium Dihydrate, $[\text{Bi}(\text{SCN})_6\text{Nd}(\text{H}_2\text{O})_3] \cdot 2\text{H}_2\text{O}$

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Abstract

In the crystal state, the title compounds form dihydrated three-dimensional polymeric complexes of general formula $[\text{Bi}(\text{SCN})_6\text{Ln}(\text{H}_2\text{O})_3] \cdot 2\text{H}_2\text{O}$, isomorphous with and with a similar structure to the $\text{LaFe}(\text{CN})_6 \cdot 5\text{H}_2\text{O}$ structure type. The distorted octahedral BiS_6 polyhedra and LnN_6O_3 polyhedra are connected by the bridging thiocyanate groups in the three-dimensional network. Six N atoms form trigonal prisms around the Ln^{III} ions with the three rectangular faces capped by three H_2O molecules. This gives La and Nd coordination polyhedra in the form of tricapped trigonal prisms. The different structural roles of the water molecules explains the literature data regarding a two-stage dehydration of the crystals. A comparison of the bond lengths in the two structures is given.