The Crystal Structure of Cobalt-Substituted Calcium Chlorapatite

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Single crystals of chlorapatite [$Ca_5(PO_4)_3Cl$] with approximately 20% substitution of Ca^{2+} by Co^{2+} have been prepared by flux techniques. A full structural analysis (space group $P6_3/m$, $a = 9.625(3)$ and $c = 6.747(1)$ Å, $V = 541.3$ Å³) indicates that the Co ion is present on the available six-coordinated cation site. As the stoichiometric chlorapatite is known to form in the ordered monoclinic structure, a detailed analysis of the halide positions along the hexagonal z axis was carried out. We conclude that the driving force for the formation of the (disordered) hexagonal structure is the tendency for Cl^- to be associated with Co^{2+}, although it is not possible to exclude a slight nonstoichiometry as a contributing factor. © 1987 Academic Press, Inc.

Introduction

The apatite structure-type, adopted by many compounds with the stoichiometry $M_5(PO_4)_3X$ (where M is a divalent metal ion and X is a halide or hydroxide ion), is typified by three compounds of calcium: fluorapatite, $Ca_5(PO_4)_3F$ (1), chlorapatite, $Ca_5(PO_4)_3Cl$ (2), and hydroxapatite, $Ca_5(PO_4)_3OH$ (3, 4).

In each of these compounds, the calcium ion occupies six- and nine-coordinated polyhedra. The structure of $Ca_5(PO_4)_3F$, crystallizing in the space group $P6_3/m$, is arranged (1) such that the F^- ions lie in sites along the hexagonal axis at 0, 0, ¼ and 0, 0, ¾ at the centers of Ca triangles. When F^- is replaced by Cl^-, the fluorine positions cannot be occupied by Cl^- because the distances to the Ca-containing polyhedra are too short. As a result, the Cl^- ions are located along the z axis at positions (0, 0,

0.06 and 0, 0, 0.56) approximately 0.3 Å from the mirror planes. Since the diameter of Cl^- is approximately one-half of the c metric, the location of a Cl^- at any of the four sites along the z axis determines the position of all other Cl^- ions in that column. The effect of a column of Cl^- ions on the rest of the structure is slight but, in perfectly stoichiometric $Ca_5(PO_4)_3Cl$, alternate columns order to lower the space group symmetry to $P2_1/b$ (2). A similar effect is found in nearly stoichiometry $Ca_5(PO_4)_3OH$, in which the OH^- groups point in "opposite" directions in alternate columns (4), again reducing the cell symmetry to monoclinic.

Very recently, the structure of Mn^{2+} partially substituted for Ca^{2+} in $Ca_5(PO_4)_3F$ has been refined by Rietveld analysis of neutron diffraction data (5). Mn substitution was found to be limited to ~⅜ atom per unit cell concentrated in the available six-coordinated cation site.

As part of a program to investigate the

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crystal chemistry of complex divalent metal phosphates, halophosphates, and hydroxy-phosphates, single crystals of a cobalt-substituted chlorapatite were prepared. This paper presents the results of our structural characterization of this material.

Experimental

During an attempt to prepare crystals of $Co_2(PO_4)Cl$ from a mixture of $Co_3(PO_4)_2$, $CoCl_2$, and NaCl (molar ratios 0.4 : 0.4 : 0.2) heated to 1100°C in a platinum crucible and cooled at 15°C/hr to 600°C, a small amount of small, well formed, pale blue, euhedral hexagonal prismatic single crystals were isolated. These crystals proved to contain a large amount of Ca^{2+}, a result of the inadvertent contamination of the flux mixture with a calcium salt.

Preliminary single-crystal X-ray diffraction and energy-dispersive X-ray analysis indicated a unit cell and stoichiometry corresponding to an apatitic-type compound with cobalt substituting for the calcium ion. (The energy-dispersive X-ray analysis was conducted on an AMR 100A scanning electron microscope using an EDAX 9100-60 analyzer capable of making full-matrix corrections using an iterative technique.) The results of the chemical analysis showed that the Ca/Co ratio was 4.1 to 1 with an estimated standard error of 0.6.

A hexagonal prism of diameter 0.06 mm and length 0.20 mm was selected for data collection. Precession photographs indicated that the space group was $P6_3/m$. A careful search of overexposed upper level photographs did not reveal the presence of any reflections that would have reduced the symmetry to monoclinic. Pure flux-grown $Ca_5(PO_4)_3Cl$ has been shown to be monoclinic (2) although it transforms to the hexagonal space group when heated above approximately 200°C (6) due to disordering of the chloride-containing column.

The lattice parameters were determined in a least-squares refinement using 26 reflections within the angular range $47° < 2\theta < 52°$; the reflections were automatically centered on a Picker FACS-I four-circle diffractometer using $MoK\alpha_1$ radiation ($\lambda = 0.70930$ Å). At 22°C the lattice parameters were found to be $a = 9.625(3)$ and $c = 6.747(1)$ Å ($V = 541.3$ Å^3), where the figures in parentheses are the standard deviations in the last reported figure.

Diffraction intensities were measured using Zr-filtered $MoK\alpha$ radiation at a takeoff angle of 1.5° with the diffractometer operating in the ω scan mode. Ten-second background counts were taken at both ends of a 1.4° θ–2θ scan corrected for dispersion. Of the 1023 independent data investigated in the angular range $2\theta < 71°$, 725 were considered observable according to the criterion $|F_o| > 1.5\sigma_F$, where σ_F is defined as $0.2|F_o| + [C + K^2B]^{1/2}/2|F_o|Lp$. C is the total scan count, k is the ratio of scanning time to the total background time, and B is the total background count. Three reflections were systematically monitored; the maximum variation in intensity observed was never greater than ±3% over the data collection period.

Intensity data were corrected for Lorentz and polarization effects, and spherical absorption corrections ($\mu = 41.9$ cm^{-1}, $MoK\alpha$) were made. The maximum relative absorption correction was 13% of $|F_o|$.

Using the positional parameters for hexagonal $Ca_5(PO_4)_3Cl$ (2), isotropic temperature factors, a $1/\sigma^2$ weighting scheme, and zerovalent scattering factors (7), the data converged to a residual of approximately 0.10 (8). At this point, an analysis of the bond lengths suggested that the Co atoms, as expected, were located in the octahedral cation site. Since the octahedral site is a crystallographic special position having a multiplicity of 6 rather than 12 (as does a general position), one-third of the atoms in this site would be Co and the other two-thirds Ca. An atom with a scattering factor

TABLE I

FRACTIONAL ATOMIC COORDINATES ($\times 10^4$) AND ANISOTROPIC THERMAL PARAMETERS FOR CO-SUBSTITUTED $Ca_5(PO_4)_3Cl^a$

Atom	10^4x	10^4y	10^4z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ca	$\frac{1}{3}$	$\frac{2}{3}$	38(2)	1.13(4)	B_{11}	0.81(4)	$\frac{1}{2}B_{11}$	0	0
Co	−43(1)	2573(1)	$\frac{1}{4}$	1.23(3)	B_{11}	0.93(3)	$\frac{1}{2}B_{11}$	0	0
P	4066(2)	3743(2)	$\frac{1}{4}$	0.72(3)	B_{11}	0.83	$\frac{1}{2}B_{11}$	0	0
O(1)	3430(5)	4921(4)	$\frac{1}{4}$	1.19(13)	B_{11}	1.25(13)	$\frac{1}{2}B_{11}$	0	0
O(2)	5916(5)	4651(5)	$\frac{1}{4}$	1.01(10)	B_{11}	2.24(16)	$\frac{1}{2}B_{11}$	0	0
O(3)	3527(4)	2662(4)	673(5)	3.00(14)	1.70(11)	1.68(12)	1.61(9)	−1.40(9)	−1.02(9)
Cl(1)	0	0	4370(11)	1.19(14)	B_{11}	7.55(13)	$\frac{1}{2}B_{11}$	0	0
Cl(2)	0	0	$\frac{1}{4}$	$6.2(1.7)^b$					

[a] Numbers in parentheses are estimated standard deviations in the last significant figures. The B's are defined by the general temperature factor $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

[b] Isotropic B.

having these properties was constructed, placed in the octahedral site, and the least-squares refinement continued. The final anisotropic refinement, which included corrections for secondary extinction and anomalous dispersion, yielded a residual R = 0.056 and R_w = 0.058 for the observed data.[1] The maximum extinction correction (9) was 15.4% of F_o for the 004 reflection.

A difference Fourier map calculated after the final refinement revealed a peak twice as large as background at $0, 0, \frac{1}{4}$. This site is the location of the F⁻ or OH⁻ ion in Ca fluor- or hydroxyapatite, respectively, but it is not occupied in $Ca_5(PO_4)_3Cl$. An atom at this site would be 2.49 Å from the octahedral cation site containing the Co atom.

[1] See NAPS document 04406 for 5 pages of supplementary material. Order From ASIS/NAPS, Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10163. Remit in advance $4.00 for microfiche copy or for photocopy, $7.75 up to 20 pages plus $0.30 for each additional page. All orders must be prepaid. Institutions and organizations may order by purchase order. However, there is a billing and handling charge for this service of $15. Foreign orders add $4.50 for postage and handling, for the first 20 pages, and $1.00 for additional 10 pages of material. Remit $1.50 for postage of any microfiche orders.

Since this distance is comparable to the 2.53 Å bond length found in $CoCl_2$ (10), another Cl atom was put into this site, with an initial occupancy of 12% and an isotropic B of 3.0. Another refinement, allowing the temperature factor and the multiplicity of this atom to vary, as well as the other normal variables, reduced the R to 0.054 and R_w to 0.056. The refined occupancy of the second Cl was 10(1)% of a fully occupied site (with an isotropic B of 6.2).

Results and Discussion

Table I lists the final atomic coordinates and anisotropic thermal parameters. The bond lengths for all of the atoms in Co-substituted $Ca_5(PO_4)_3Cl$ are presented in Table II with a comparison to the lengths found in pure $Ca_5(PO_4)_3Cl$ (2). There is no significant difference between the cell metric of Co-substituted apatite and pure $Ca_5(PO_4)_3Cl$ in the hexagonal plane, but there is a significant shrinkage of the c axis (which is not surprising, since Co has a smaller radius than Ca). As a result, there are only slight differences in bond distances. There is more shrinkage of bond lengths in the octa-

		I	II[b]
Ca polyhedron			
Ca–O(1)	3×	2.397(3)	2.398
Ca–O(2)	3×	2.445(3)	2.447
Ca–O(3)	3×	2.798(4)	2.789
Co polyhedron			
Co–O(2)		2.282(4)	2.295
Co–O(3)	2×	2.321(3)	2.336
Co–Cl(2)	2×	2.498(2)	
Co–O(3)	2×	2.536(4)	2.539
Co–Cl(1)	2×	2.798(4)	2.801
P polyhedron			
P–O(3)	2×	1.527(3)	1.529
P–O(1)		1.535(4)	1.536
P–O(2)		1.542(4)	1.542
Cl(1) polyhedron			
Cl(1)–Co	3×	2.798(4)	2.801
O(1) polyhedron			
O(1)–P		1.535(4)	1.536
O(1)–Ca	2×	2.397(3)	2.398
O(2) polyhedron			
O(2)–P		1.542(4)	1.542
O(2)–Co		2.282(4)	2.295
O(2)–Ca	2×	2.445(3)	2.447
O(3) polyhedron			
O(3)–P		1.527(3)	1.529
O(3)–Co		2.321(3)	2.336
Cl(2) polyhedron			
Cl(2)–Co	3×	2.498(2)	

[a] Numbers in parentheses are eds's in the last reported figure.
[b] Reference (2).

hedral site, supporting the premise that the Co is concentrated there.

The primary difference between the two compounds is the distribution of Cl atoms along the z axis. Figure 1 is a projection of the Cl and neighboring atoms along this axis including all of the anion sites. The space group $P6_3/m$ has a mirror at 0 and $\frac{1}{2}$ in z, and the location of a Cl atom at (0, 0, 0.44) causes another Cl atom to appear at (0, 0, 0.56). A similar situation occurs at the mirror at $z = 0$. The distance between these two atoms is only 0.85 Å, obviously too

close for Cl atoms to occupy both positions.

In stoichiometric $Ca_5(PO_4)_3Cl$, in which the Cl atoms order perfectly, one column will have atoms only at $z = 0.44$ and 0.94, and an adjacent column would have Cl atoms at $z = 0.06$ and 0.56. This perfect ordering doubles the unit cell in the b direction and lowers the space group symmetry to $P2_1/b$. When these crystals are heated (6), thermal vibrations destroy the ordering and the now random Cl atoms yield the higher symmetry space group $P6_3/m$. In Co-substituted $Ca_5(PO_4)_3Cl$, a Cl atom at the second site ($z = \frac{1}{4}$) forces the sites at $z = 0.06$, 0.44, 0.56, and 0.94 to be empty in that particular column. Since the special position also has an atom at $z = \frac{3}{4}$, charge balance is maintained in that particular region of the crystal. Thus, Fig. 1 shows all of the sites for Cl atoms are constrained to be one-half of a unit cell apart in the z direction.

It is interesting to note that both the crystals grown in this study and the Mackie study (2) were prepared under similar conditions, but the structure of the Co-substituted compound is disordered at room temperature while pure $Ca_5(PO_4)_3Cl$ is not. Chlorapatites can be prepared with as much as 15% deficiency in chlorine (11), in which charge balance is maintained by eliminating the proper amount of Ca atoms from either cation site. Since some columns of chlorine atom sites now have vacancies, the ordering mechanism, as described by Mackie et al. (2), cannot produce long-range ordering and these anion-deficient chlorapatites have the space group $P6_3/m$ (the disordered structure). The chlorine content of the crystals used in this study was investigated by energy-dispersive X-ray analysis, which indicated that the crystals had surplus chlorine. However, the quality of this analysis is dubious, since an analysis for total oxygen could not be made.

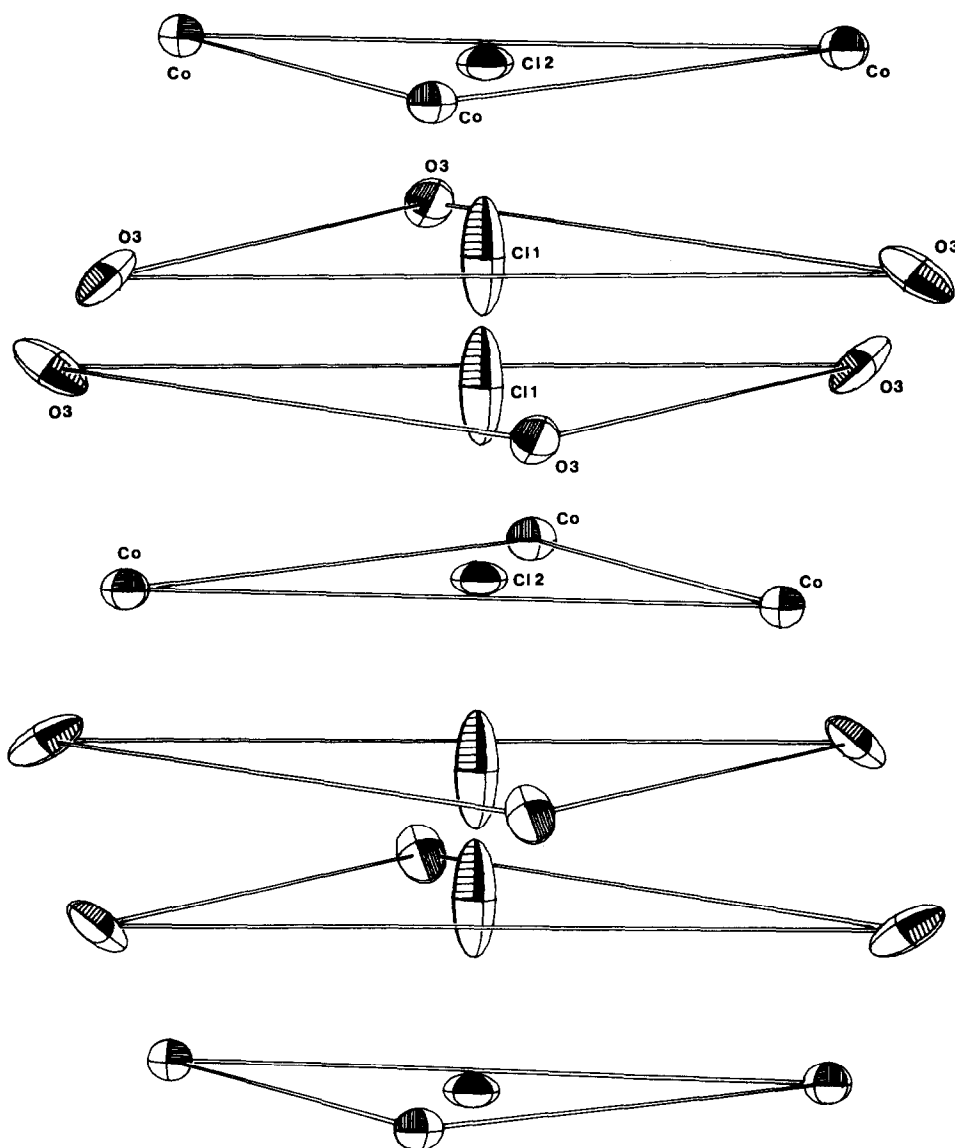As the ordered apatite structure has two

FIG. 1. A portion of the structure of Co-substituted $Ca_5(PO_4)_3Cl$ viewed perpendicular to the z axis showing all of the possible sites for the Cl^- ion. In any particular column the chlorine atoms are constrained by steric conditions to be one-half of a unit cell apart. The size of Cl(2) has been reduced for clarity.

incompatible sites for the Cl atoms, a suffi-cient driving force for this disorder is most certainly the Co atom in the six-coordi-nated site. Chlorine atoms undoubtably tend to occupy the 0, 0, $\frac{1}{4}$ site when a Co atom is in an octahedral site near that par-ticular anion site. This probable linking of Co and Cl atoms prevents the structure from ordering in the manner that pure Ca_5 $(PO_4)_3Cl$ does. This driving force alone should be sufficient to disorder the struc-ture, whether a deficiency in chlorine is

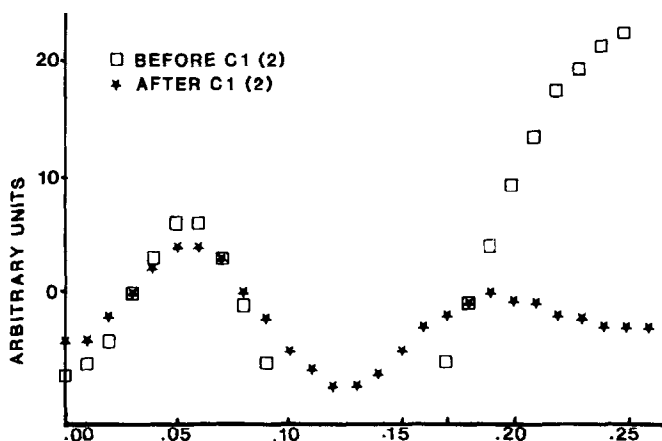FIG. 2. A plot of the electron density along the z axis in the Fourier difference map for Co-substituted $Ca_5(PO_4)_3Cl$ before ($\square$) and after (*) the addition of $Cl(2)$.

present or not. The occupancy factors for both Cl sites were varied in the final cycles of refinement. The final occupancy factors were 0.79(1) for Cl(1) and 0.10(2) for Cl(2), indicating an 11% deficiency in total chlorine in the structure.

To investigate the possibility that additional sites along the z axis might contain chlorine, a difference Fourier map was calculated after the final refinement. Figure 2 is a graph of the electron density calculated every 0.01 of a unit cell along z. The magnitude is in 0.001 of the height of the strongest peak in the Fourier map (not the difference Fourier map). The two sets of points represent the density (a) before Cl(2) was added to the refinement and (b) after the final refinement. As can be seen, the need for the addition of Cl(2) is obvious; however, after the final refinement, there is no location that satisfactorily represents an additional Cl atom. The maximum peak at $z = 0.06$ is approximately one-third the height of the largest peak in the final difference map, certainly no higher than the negative ripples in the map.

The deficiency in chlorine determined from the occupancy factors is unlikely to be the actual chlorine deficiency in this struc-

ture. It is believed that the large temperature factors found for the chlorine atom indicate that there is a large amount of movement in their positions which is not being adequately accounted for in the least-squares calculations of occupancy and temperature factors (particularly in the anisotropic B_{33} component). Without an accurate determination of the composition of the crystal on which the diffraction data was collected, the true deficiency of the chlorine cannot be determined.

Acknowledgments

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