that $Na_{0.5}Bi_{0.5}MoO_4$ and $Na_{0.32}Bi_{0.56}\square_{0.18}MoO_4$ both adopt the scheelite structure with $Na^+$, $Bi^{3+}$ and vacancies randomly occupying the eight coordinate '*A*' site. Similarly, on the basis of powder X-ray diffraction data, $Na_{0.5}M'_{0.5}MoO_4$ ($M'$ = Ce, La) have been shown to be isostructural with scheelite. Presumably, a deficiency of Na in these structures can also be compensated for by excess Ce or La and vacancies in a manner similar to the Bi-containing compound.

An examination of Table 3 shows the similarity of the structures examined herein. All four structures have very similar '*B*' ($MoO_4$) and '*A*' coordination environments. This is not surprising in light of the similarities in cation size [$Na^+$ 1.16, $Bi^{3+}$ 1.11, $Ce^{3+}$ 1.14, $La^{3+}$ 1.18 Å (Huheey, 1972)]. For comparison, *A*—O and *B*—O distances for $PbMoO_4$ are given in Table 3.

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# Structure Refinement of $Co_3(OH)_2(PO_3OH)_2$ and $Co[PO_2(OH)_2]_2.2H_2O$

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**Abstract.** Tricobalt dihydroxide bis(hydrogenphosphate), $Co_3(OH)_2(PO_3OH)_2$, $M_r = 402.77$, monoclinic, $P2_1/c$, $a = 7.524\,(2)$, $b = 7.512\,(2)$, $c = 7.395\,(2)$ Å, $\beta = 117.88\,(2)°$, $V = 369.5\,(1)$ Å$^3$, $Z = 2$, $D_x = 3.621$ Mg m$^{-3}$, $\lambda$(Mo $K\alpha$) = 0.71073 Å, $\mu = 6.9$ mm$^{-1}$, $F(000) = 390$, room temperature, $wR(F) = 0.027$ for 2049 reflections. The structure is closely related to that of lazulite, $MgAl_2(OH)_2(PO_4)_2$. Cobalt bis(dihydrogenphosphate) dihydrate, $Co[PO_2(OH)_2]_2.2H_2O$, $M_r = 288.94$, monoclinic, $P2_1/n$, $a = 7.268\,(2)$, $b = 9.886\,(3)$, $c = 5.331\,(1)$ Å, $\beta = 94.86\,(2)°$, $V = 381.7\,(1)$ Å$^3$, $Z = 2$, $D_x = 2.514$ Mg m$^{-3}$, $\lambda$(Mo $K\alpha$) = 0.71073 Å, $\mu = 2.56$ mm$^{-1}$, $F(000) = 290$, room temperature, $wR(F) = 0.028$ for 1678 reflections. A member of the $M[PO_2(OH)_2]_2.2H_2O$-type structures with $M$ = Mg, Mn, Fe, Co or Cd.

**Introduction.** In connection with investigations of the coordination chemistry of transition-metal atoms towards O atoms, syntheses in parts of the system $CoO–P_2O_5–H_2O$ were performed. As a result, the crystal structure of $Co(PO_3OH).H_2O$ was recently determined (Effenberger, Parik, Pertlik & Rieck, 1991); the crystal structures of $Co_3(OH)_2(PO_3OH)_2$ and $Co[PO_2(OH)_2]_2.2H_2O$ were presented at the common meeting of the 'Arbeitsgemeinschaft Kristallographie' and the 'Vereinigung für Kristallographie' in Münich, Germany (Effenberger, 1991). In the meantime a paper about the structural investigation and magnetic characterization of $Co_3(OH)_2(PO_3OH)_2$ was published by Pizarro, Villeneuve, Hagenmuller & Le Bail (1991). Because their structure determination was based only on powder X-ray ($X_p$) and powder neutron ($N_p$) diffraction data a comparison with single-crystal X-ray diffraction data ($X_s$) seemed to be worthwhile. The lattice parameters of $Co[PO_2(OH)_2]_2.2H_2O$ have been given by Vasić, Prelesnik, Čurić & Herak (1985); in addition they mentioned the isotypism with $M[PO_2(OH)_2]_2.2H_2O$,

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$M$ = Mg, Fe, Mn and Cd (Hinsch, 1985; Guse, Klaska, Saalfeld & Adiwidjaja, 1985; Vasić *et al.*, 1985; Averbuch-Pouchot, Durif, Guitel, Tordjman & Laügt, 1973).

**Experimental.** For synthesis *cf.* Effenberger *et al.* (1991). Details of data collection and structure refinements are given in Table 1. Laue group and extinction rules from Weissenberg photographs, lattice parameters and X-ray intensities from a Stoe AED2 four-circle diffractometer. Intensities corrected for Lorentz and polarization effects; complex neutral atomic scattering functions from *International Tables for X-ray Crystallography* (1974, Vol. IV). Atomic coordinates of Co atoms from Patterson summations, subsequent Fourier and difference Fourier summations showed the P-, O- and H-atom positions.

For $Co_3(OH)_2(PO_3OH)_2$ the labelling of O atoms is in accordance with that in lazulite (Lindberg & Christ, 1959; Giuseppetti & Tadini, 1983). Their unit cell is maintained: in the present case the $P2_1/c$ setting represents the reduced cell. As was mentioned by Sieber, Tillmanns & Hofmeister (1987), for lazulite itself the $P2_1/n$ setting corresponds to the reduced unit cell. For $Co[PO_2(OH)_2]_2.2H_2O$ the labelling of atoms corresponds to that of the isotypic Mg and Fe compounds (Hinsch, 1985; Guse *et al.*, 1985).

During final structure refinements isotropic displacement parameters for the H atoms and anisotropic ones for the other atoms were allowed to vary. Final structure parameters are in Table 2.* Hydroxyl O and H atoms are indicated by suffix $h$, those of the water molecule by $w$.

Table 1. *Summary of X-ray intensity measurements and structure refinements*

Stoe AED2 four-circle diffractometer, Mo tube, graphite monochromator; calculations on an Eclipse S/140 computer, program system *STRUCSY* (Stoe & Cie, 1984).

| | $Co_3(OH)_2(PO_3OH)_2$ | $Co[PO_2(OH)_2]_2.2H_2O$ |
|---|---|---|
| Crystal dimensions (mm) | 0.08 × 0.12 × 0.27 | 0.13 × 0.16 × 0.38 |
| Colour | Light wine-red | Light pink |
| Reflections for cell parameters | 75 | 75 |
| $2\theta$ range (°) | 42.6 to 53.2 | 41.8 to 52.3 |
| Absorption correction | 12 $\psi$ scans | 10 $\psi$ scans |
| Transmission factors | 0.346 to 0.462 | 0.555 to 0.660 |
| Step width, $2\theta/\omega$ scan (°) | 0.96 + $K\alpha$ dispersion | 0.93 + $K\alpha$ dispersion |
| Background correction (°) | Twice 0.24 | Twice 0.21 |
| Step time (° $min^{-1}$) | 1.2 to 3.6 | 1.2 to 3.6 |
| $2\theta$ max (°) | 80 | 70 |
| Intensity variation (%) | ±1.1 | ±2.9 |
| Measured reflections | 4858 ($+h$, $\pm k$, $\pm l$) | 5240 ($\pm h$, $\pm k$, $\pm l$) |
| Unique reflections | 2304 | 1678 |
| Data with $F_o > 3\sigma(F_o)$ | 2049 | 1490 |
| $R_{int}$ | 0.10 | 0.11 |
| Variables | 79 | 78 |
| Extinction parameter $g$ (Zachariasen, 1967) | 3.5 (3) × $10^{-5}$ | 2.0 (1) × $10^{-4}$ |
| Final difference Fourier map (e Å$^{-3}$) | −2.84 to 2.19 | −1.78 to 0.70 |
| $R$, $wR$; $w = [\sigma(F_o)]^{-2}$ | 0.036, 0.027 | 0.033, 0.028 |
| $R$, $wR$ for all reflections | 0.042, 0.028 | 0.037, 0.028 |

Table 2. *Positional parameters and equivalent isotropic displacement parameters* (Å$^2$)

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

| | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| $Co_3(OH)_2(PO_3OH)_2$ | | | | |
| Co(1) | 0 | 0 | 0 | 0.0097 (1) |
| Co(2) | 0.74331 (3) | 0.27465 (3) | 0.01793 (3) | 0.0103 (1) |
| P | 0.23456 (6) | 0.38207 (5) | 0.23612 (5) | 0.0086 (1) |
| O(1) | 0.1830 (2) | 0.5145 (2) | 0.3587 (2) | 0.0136 (5) |
| O(2) | 0.3262 (2) | 0.4715 (2) | 0.1138 (2) | 0.0118 (5) |
| O(3) | 0.0563 (2) | 0.2651 (2) | 0.1061 (2) | 0.0135 (5) |
| $O_h$(4) | 0.4096 (2) | 0.2545 (2) | 0.3912 (2) | 0.0139 (5) |
| $O_h$(5) | 0.7456 (2) | 0.3694 (2) | 0.2756 (2) | 0.0112 (5) |
| $H_h$(1) | 0.382 (5) | 0.196 (4) | 0.459 (5) | 0.051 (9) |
| $H_h$(2) | 0.664 (4) | 0.427 (3) | 0.253 (3) | 0.010 (5) |
| $Co[PO_2(OH)_2]_2.2H_2O$ | | | | |
| Co | $\frac{1}{2}$ | $\frac{1}{2}$ | $\frac{1}{2}$ | 0.0139 (1) |
| P | 0.83784 (5) | 0.28523 (4) | 0.74724 (6) | 0.0145 (2) |
| O(1) | 0.6452 (1) | 0.3316 (1) | 0.6619 (2) | 0.0200 (5) |
| O(2) | 0.8641 (2) | 0.1341 (1) | 0.7396 (2) | 0.0198 (5) |
| $O_h$(3) | 0.9686 (2) | 0.3567 (1) | 0.5706 (2) | 0.0276 (6) |
| $O_h$(4) | 0.8872 (2) | 0.3383 (1) | 0.0220 (2) | 0.0240 (6) |
| $O_w$(5) | 0.3002 (2) | 0.4633 (1) | 0.7604 (2) | 0.0193 (5) |
| $H_w$(1) | 0.342 (3) | 0.431 (3) | 0.892 (5) | 0.050 (7) |
| $H_w$(2) | 0.260 (3) | 0.534 (2) | 0.799 (4) | 0.036 (6) |
| $H_h$(3) | 0.068 (4) | 0.366 (2) | 0.645 (4) | 0.050 (7) |
| $H_h$(4) | 0.950 (4) | 0.292 (3) | 0.098 (6) | 0.075 (10) |

**Discussion.** Selected interatomic distances and bond angles are compiled in Table 3, distortion parameters of the coordination polyhedra around Co and P in Table 4. The atomic arrangement in $Co_3(OH)_2(PO_3OH)_2$ is related to that in lazulite, $MgAl_2(OH)_2(PO_4)_2$: the Mg- and Al-atom positions are occupied by Co atoms; one O atom which is [2] coordinated by one Al and one P atom in lazulite acts as the donor atom of the new hydrogen bond which serves as charge balance for $Al^{III}/Co^{II}$ exchange. Minor shifts of the atomic positions result from this substitution, but the connection scheme is maintained: one $Co(1)(O_h)_2O_4$ octahedron shares opposite faces with $Co(2)(O_h)_3O_3$ octahedra forming $Co_3(O_h)_6O_6$ groups. These groups are corner-connected *via* $O_h$ atoms to corrugated $Co_3(O_h)_4O_6$ layers in (100), which are linked by phosphate groups and by hydrogen bonds (Fig. 1). Topologically related is the orthorhombic compound $CuFe_2(OH)_2(AsO_4)_2$ with fourfold cell content but larger periodicity for the rugged sheets (Effenberger, 1988). In $Co[PO_2(OH)_2]_2.2H_2O$ isolated $CoO_4(O_w)_2$ octahedra are corner-connected with four phosphate groups to form layers; the two $O_h$ atoms are not involved in the

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* Lists of anisotropic displacement parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55283 (21 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: BX0567]

Table 3. *Selected interatomic distances* (Å) *and bond angles* (°)

$\mathrm{Co_3(OH)_2(PO_3OH)_2}$

| Co(1) | O(1) | O(3) | O$_h$(5) |
|---|---|---|---|
| O(1) | 2.085 (1) | 80.16 (5)<br>99.84 (5) | 78.48 (5)<br>101.53 (5) |
| O(3) | 2.700 (2)<br>3.209 (2) | 2.109 (1) | 78.66 (5)<br>101.34 (5) |
| O$_h$(5) | 2.647 (2)<br>3.241 (2) | 2.668 (2)<br>3.256 (2) | 2.100 (1) |

| P | O(1) | O(2) | O(3) | O$_h$(4) |
|---|---|---|---|---|
| O(1) | 1.513 (1) | 112.29 (8) | 111.28 (8) | 108.68 (7) |
| O(2) | 2.524 (2) | 1.526 (1) | 113.02 (8) | 103.88 (7) |
| O(3) | 2.498 (2) | 2.535 (2) | 1.513 (1) | 107.21 (7) |
| O$_h$(4) | 2.529 (2) | 2.461 (2) | 2.505 (2) | 1.599 (1) |

| Co(2) | O(1) | O(2) | O(3) | O$_h$(4) | O$_h$(5) | O$_h$(5) |
|---|---|---|---|---|---|---|
| O(1) | 2.118 (1) | 177.54 (5) | 78.92 (5) | 96.10 (5) | 91.93 (5) | 77.71 (5) |
| O(2) | 4.211 (2) | 2.093 (1) | 99.97 (5) | 84.67 (5) | 90.45 (5) | 99.93 (5) |
| O(3) | 2.700 (2) | 3.235 (2) | 2.131 (1) | 170.32 (5) | 101.64 (5) | 78.16 (5) |
| O$_h$(4) | 3.244 (2) | 2.922 (2) | 4.358 (2) | 2.242 (1) | 86.73 (5) | 92.72 (5) |
| O$_h$(5) | 2.981 (2) | 2.925 (2) | 3.223 (2) | 2.936 (2) | 2.027 (1) | 169.52 (5) |
| O$_h$(5) | 2.647 (2) | 3.211 (2) | 2.668 (2) | 3.144 (2) | 4.110 (2) | 2.100 (1) |

| Donor | Hydrogen | Acceptor | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|---|---|
| O$_h$(4) | H$_h$(1) | O(2) | 0.77 (4) | 1.88 (4) | 2.637 (2) | 172 (1) |
| O$_h$(5) | H$_h$(2) | O(2) | 0.70 (3) | 2.28 (3) | 2.906 (2) | 150 (1) |
| O$_h$(5) | H$_h$(2) | O$_h$(4) | | 2.64 (3) | 3.148 (2) | 132 (2) |

O(2)—H$_h$(2)—O$_h$(4) 72 (1)

$\mathrm{Co[PO_2(OH)_2]_2.2H_2O}$

| Co | O(1) | O(2) | O$_h$(5) |
|---|---|---|---|
| O(1) | 2.116 (1) | 87.89 (4)<br>92.11 (4) | 86.79 (4)<br>93.21 (4) |
| O(2) | 2.929 (1)<br>3.039 (1) | 2.105 (1) | 89.14 (4)<br>90.86 (4) |
| O$_w$(5) | 2.912 (2)<br>3.080 (2) | 2.967 (2)<br>3.012 (1) | 2.123 (1) |

| P | O(1) | O(2) | O$_h$(3) | O$_h$(4) |
|---|---|---|---|---|
| O(1) | 1.507 (1) | 114.19 (7) | 106.11 (7) | 108.26 (6) |
| O(2) | 2.530 (1) | 1.507 (1) | 110.32 (7) | 109.74 (6) |
| O$_h$(3) | 2.453 (2) | 2.519 (2) | 1.563 (1) | 107.99 (7) |
| O$_h$(4) | 2.492 (1) | 2.516 (2) | 2.533 (2) | 1.569 (1) |

| Donor | Hydrogen | Acceptor | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|---|---|
| O$_w$(5) | H$_w$(1) | O(2) | 0.81 (2) | 1.96 (2) | 2.733 (1) | 161 (3) |
| O$_w$(5) | H$_w$(2) | O$_h$(4) | 0.79 (2) | 1.96 (2) | 2.704 (2) | 158 (3) |
| O$_h$(3) | H$_h$(3) | O$_w$(5) | 0.80 (3) | 2.00 (3) | 2.744 (2) | 156 (3) |
| O$_h$(4) | H$_h$(4) | O(1) | 0.74 (3) | 1.89 (3) | 2.580 (2) | 157 (4) |

H$_w$(1)—O$_w$(5)—H$_w$(2) 104 (4)
O(2)···O$_w$(5)···O$_h$(4) 84.64 (4)

Table 4. *Distortion parameters for the coordination polyhedra around* Co *and* P

$$\mathrm{DI}_d = \Big(\sum_{i=1}^{n_1} |d_i - d_m|\Big)/n_1 d_m;\ \mathrm{DI}_{\angle} = \Big(\sum_{i=1}^{n_2} |\angle_i - \angle_m|\Big)/n_2 \angle_m;$$

$$\mathrm{DI}_e = \Big(\sum_{i=1}^{n_2} |e_i - e_m|\Big)/n_2 e_m.$$

| | $\mathrm{Co_3(OH)_2(PO_3OH)_2}$ | | | $\mathrm{Co[PO_2(OH)_2]_2.2H_2O}$ | |
|---|---|---|---|---|---|
| | Co(1) | Co(2) | P | Co | P |
| DI$_d$ | 0.0041 | 0.0215 | 0.0200 | 0.0030 | 0.0192 |
| DI$_\angle$ | 0.1211 | 0.0804 | 0.0256 | 0.0229 | 0.0181 |
| DI$_e$ | 0.0954 | 0.0628 | 0.0082 | 0.0180 | 0.0092 |

*d*, ∠, *e* signify Co/P—O bond distance, O—Co/P—O angle and O—O edge within the relevant polyhedron; index *i* indicates individual values, index *m* the mean value for the polyhedron. $n_1$ and $n_2$ are 4 and 6 for the phosphate tetrahedra and 6 and 12 for the cobalt octahedra. For reference *cf.* Baur (1974) and Wildner (1990, 1992).

Co coordination. Co[PO$_2$(OH)(O$_h$)]$_2$(O$_w$)$_2$ layers are formed in ($\bar{1}$01) which are exclusively linked by the three remaining hydrogen bonds (Fig. 2).

The Co atoms in the two title compounds are octahedrally coordinated to O, O$_h$ and O$_w$ atoms, respectively. Average ⟨Co—O⟩ bond distances vary from 2.027 to 2.131 Å. Worth mentioning is the long Co(2)—O$_h$(4) bond distance in $\mathrm{Co_3(OH)_2(PO_3OH)_2}$, balancing bond valences at the O$_h$(4) atom due to the new hydrogen bond as compared to the lazulite structure. As pointed out by Wildner (1990, 1992), the angular distortions of both crystallographically different Co atoms in $\mathrm{Co_3(OH)_2(PO_3OH)_2}$ are peculiarly large and result from face-connection of cobalt octahedra (Table 4). As a consequence, the O—O edges belonging to shared faces are shorter than the unshared ones. The Co(O$_h$)$_2$O$_4$ octahedron in Co[PO$_2$(OH)$_2$]$_2$.2H$_2$O has a smaller DI$_d$ (for definition see Table 4) as compared with the four other known isotypic compound: for *M* = Mg, Mn, Fe and Cd DI$_d$ = 0.0176, 0.0216, 0.0287 and 0.0171, respectively. This is surprising because the Co$^{\mathrm{II}}$ ion has the electron configuration [Ar]3$d^7$ and therefore a distortion in an octahedral complex should be expected (Jahn–Teller effect).

The two compounds under discussion involve protonated phosphate groups. The distinct bond distances agree with the number of O atoms in the phosphate tetrahedra which are donor atoms in hydrogen bonds. ⟨P—O⟩ and ⟨P—$O_h$⟩ are longer in the $PO_3OH$ group than in $PO_2(OH)_2$. The angles O—P—O are definitely larger than O—P—$O_h$ and $O_h$—P—$O_h$. The same trends have been found by Corbridge (1971), Baur (1974), Ferraris & Ivaldi (1984) and Ichikawa (1987). The distortion parameters $DI_d$ and $DI_L$ (see Table 4) in $Co_3(OH)_2(PO_3OH)_2$ are larger, those for $DI_L$ and $DI_e$ in $Co[PO_2(OH)_2]_2.2H_2O$ are smaller than average values given by Ichikawa (1987) for $PO_3OH$ and $PO_2(OH)_2$ groups.

The hydrogen bonds were verified experimentally by location of the H atoms. The bifurcated hydrogen bond in $Co_3(OH)_2(PO_3OH)_2$ is less pronounced than in lazulite. Interesting is the $O_h(4)$—$H_h(4)\cdots O(1)$ bond length in $Co[PO_2(OH)_2]_2.2H_2O$ of only 2.580 Å (within the layer). Similar short hydrogen bonds have been mentioned for the isotypic compounds. In the protonated $Co^{II}$ phosphate $Co_7(PO_3OH)_4(PO_4)_2$, Lightfoot & Cheetham (1988) described an extremely short O—H···O bond distance of 2.448 (1) Å for a definitely not centrosymmetric hydrogen bond.

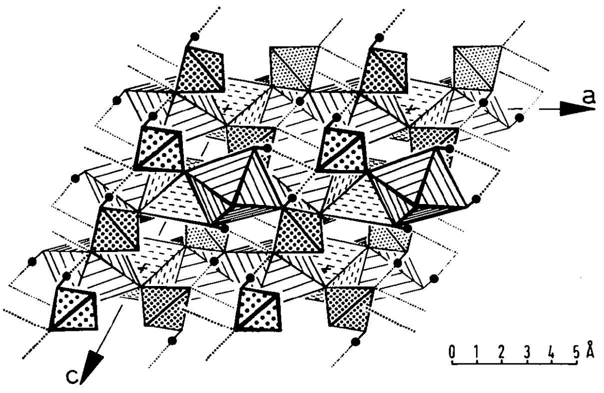

Fig. 1. The structure of $Co_3(OH)_2(PO_3OH)_2$ in a projection on (010).

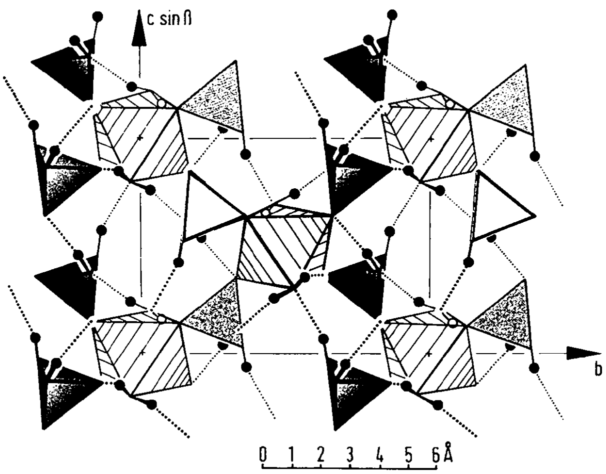

Fig. 2. The structure of $Co[PO_2(OH)_2]_2.2H_2O$ in a projection parallel to [100].

To compare interatomic distances determined from $X_s$ and $N_p$ in correlation with their standard deviations in the compound $Co_3(OH)_2(PO_3OH)_2$ seems to be of general technical interest. Co—O bond distances vary by up to 0.025 Å (average 0.013 Å), P—O bond distances by up to 0.018 Å (average 0.008 Å), and O—O edges by up to 0.038 Å (average 0.010 Å). The differences of the calculated interatomic distances for these two refinements do not exceed four times the estimated standard deviations. The differences in bond angles exceed only in a few cases twice the e.s.d.: the average deviation is 0.46°, maximum 1.27°. Owing to the poorer reliability of $X_p$ as compared to the $N_p$ data, the deviation for the results of the $X_p$ refinement as compared to $X_s$ is larger except for Co—O distances: these vary only up to 0.025 Å (average 0.010 Å), P—O differs up to 0.035 Å (average 0.022 Å), and O—O up to 0.053 Å (average 0.022 Å). The largest bond-angle difference was calculated for an O—P—O angle (2.70°); the average difference is 0.89°.

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