Investigation on pseudosymmetry, twinning and disorder in crystal structure determinations: Ba(H$_2$O)M_2^{III}[PO$_3$(OH)]$_4$ (M=Fe, V) as examples

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ABSTRACT

Twinning commonly occurs in monoclinic crystals with dimensionally similar a and c axes and results in pseudo-orthorhombic symmetries with overlapping diffractions. For example, twinning in the new synthetic compound Ba(H$_2$O)Fe$_2$[PO$_3$(OH)]$_4$, which varies in space group from $P2_1$ to $P2_1/c$ with approximately equal a and c axial lengths, gives rise to a pseudosymmetry of $C222_1$. Similarly, the related compound Ba(H$_2$O)V$_2$[PO$_3$(OH)]$_4$ is commonly twinned and varies in space groups as well, arising from ordered to disordered distributions of the barium cations and water molecules in the cavities. Moreover, analyses of these and other twinned structures show that the small average standard uncertainty of bond distances is a sensitive criterion for structure determinations, especially for those involving crystal twinning as well as order–disorder. A proper structure determination leads to small standard uncertainties of the atomic displacement parameters, which further result in the small standard uncertainties of bond distances.

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1. Introduction

The symmetry (i.e. crystal system and space group) of a new crystalline compound is commonly determined by use of the X-ray diffraction technique on the basis of reflection conditions and statistical analysis of equivalent reflections. However, inherent limitation of the X-ray diffraction technique, such as Friedel's rule, i.e. $|F(hkl)|^2=|F(\bar{h}\bar{k}\bar{l})|^2$, makes this process not straightforward. Particularly, crystal twinning commonly occurs and results in diffraction spots of different domains being partially or wholly coincident in the reciprocal space, which in turn gives rise to pseudosymmetry. For example, the diffraction behavior of apparent superlattice reflections observed in electron diffraction patterns of modulated calcite and dolomite has been interpreted to arise from microscopic (104) twin domains [1].

Orthorhombic, monoclinic and triclinic crystal systems are characterized by symmetrically nonequivalent axes **a**, **b** and **c**. However, dimensional equality between two or among all three axes in these crystal systems is not excluded. For example, a search of Inorganic Crystal Structure Database (ICSD) [2] reveals that more than 260 monoclinic compounds possess dimensionally equal a and c axes or have differences within 0.5%. Crystal twinning is commonly observed in those compounds with similar

axial lengths [3]. Mathematically, a C-centered orthorhombic cell has a monoclinic Niggli reduced cell with equal a- and c-axis. Therefore, a monoclinic cell with dimensionally equal a and c axes can be falsely transformed to a pseudo-orthorhombic one where twinning by pseudomerohedry occurs. In this case, standard uncertainty of unit cell parameters [4,5] is not useful for determining whether axial lengths are equal or not. Moreover, twin domains significantly affecting equivalent reflections' intensities and reflection conditions hamper with determination of the real space group.

An interesting example of this type is the compound (NH$_4$)In [PO$_3$(OH)]$_2$, which was reported by Mao et al. [6] to have the following cell parameters: $P2_1/c$, $a=9.6004(4)$ Å, $b=8.2820(4)$ Å, $c=9.6693(3)$ Å, $\beta=116.205(4)°$, $V=689.79$ Å^3. A concurrent but independent study of this compound by Filaretov et al. [7] gave $P2_1/c$, $a=9.6651(1)$ Å, $b=8.2763(1)$ Å, $c=9.5964(1)$ Å, $\beta=116.15(1)$, $V=689.06$ Å^3. Obviously, the cell parameters reported by these two studies are in reasonable agreement. Closer examination reveals that the a-axis in the former is slightly shorter than the c-axis, while opposite is true in the latter (see discussion below), even though the same space group $P2_1/c$ was adopted by both studies. Conventionally, if the compound in the setting selected by the former study has a space group $P2_1/c$, it should have a space group $P2_1/a$ in the setting of the latter study (i.e. switching the a and c axes). Recently, we have investigated a twinned crystal (twinning by pseudomerohedry) of this compound (NH$_4$)In(PO$_3$(OH))$_2$ and note that structure refinements converged in four different space groups (Table 1).

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Table 1
Comparison of structure refinements of $(NH_4)In[PO_3(OH)]_2$ in four space groups.

Space group	$C222_1$	$P2_1$	$P2_1/a$	$P2_1/c$
Cell parameters (Å, deg., Å³)	$a' = 10.1850(6)$	$a = 9.6125(5)$	$a = 9.6125(5)$	$a = 9.6125(5)$
	$b' = 16.3055(9)$	$b = 8.2358(6)$	$b = 8.2358(6)$	$b = 8.2358(6)$
	$c' = 8.2358(6)$	$c = 9.6125(5)$	$c = 9.6125(5)$	$c = 9.6125(5)$
	$V' = 1367.74$	$\beta = 116.019(3)$	$\beta = 116.019(3)$	$\beta = 116.019(3)$
		$V = 683.86$	$V = 683.86$	$V = 683.86$
R_{int}, $R_{\sigma(I)}$	0.0183, 0.0256	0.0173, 0.0281	0.0186, 0.0268	0.0186, 0.0268
S, Wa, Wb[a]	1.091, 0.0174, 133.26	0.987, 0.0278, 0.0	0.987, 0.0216, 0.0	0.988, 0.0215, 0.0
R_1, wR_2	0.0572, 0.1426	0.0197, 0.0474	0.0170, 0.0392	0.0170, 0.0392
$N_{all}(N_{gt})$, N_{para}	2124 (1969), 75	3181 (2927), 137	2193 (2070), 130	2193 (2070), 130
LDPH[b]	3.190, −5.117	0.792, −0.617	0.742, −0.539	0.799, −0.623
ASUBD[c]	$\sigma(\text{In–O}) = 0.0138$ Å	$\sigma(\text{In–O}) = 0.009$ Å	$\sigma(\text{In–O}) = 0.0019$ Å	$\sigma(\text{In–O}) = 0.0019$ Å
	$\sigma(\text{P–O}) = 0.0162$ Å	$\sigma(\text{P–O}) = 0.0108$ Å	$\sigma(\text{P–O}) = 0.0023$ Å	$\sigma(\text{P–O}) = 0.0024$ Å

[a] WGHT parameters (Wa and Wb) denote the weighting scheme of $W = 1/[\sigma^2(Fo^2) + (Wa \times P)^2 + Wb \times P]$, where $P = (Fo^2 + 2Fc^2)/3$.
[b] LDPH denotes the largest difference electron-density peak/hole (e/Å³).
[c] ASUBD is the average standard uncertainty of bond distances. Note that P–O bond distances in the space group $C222_1$ are anomalous large owing to positional disorder.

These various results apparently arise from the fact that this compound has dimensionally similar a- and c-axis in the true monoclinic cells (Table 1). In this regard, twinning involving monoclinic crystals with special angles (i.e. β is close to 120° with $a \approx c$ or $\beta \approx 90°$) has been extensively investigated [8]. A monoclinic twinned crystal, which has approximately equal a- and c-axis lengths but its reflections split partially or wholly at high diffraction angles, has also been fully studied [3]. A number of characteristic warning signs for twinning, including an unusually long axis, low value of $|E^2 - 1|$, and large weight parameters, etc., have been identified by previous studies [8,9]. Twinning by pseudomerohedry with special metric only (i.e. $a = c$ but $\beta \neq 90°$ or $\neq 120°$) is expected to be common but has been reported only occasionally owing to difficulty of detection [9]. To the best of our knowledge, only two cases of twinning by pseudomerohedry that gives rise to a pseudo-orthorhombic cell ($C222_1$) from real space groups of $P2_1/c$ or $P2_1$ have been reported [9,10]. For example, the recognition of the real monoclinic space group in one of these cases took 30 years after the first report of the pseudo-orthorhombic cell [10]. Therefore, twinning in monoclinic crystals with equal a- and c-axis is a significant challenge in structure determinations.

Herein, we report on single-crystal X-ray structural analyses of a new synthetic compound, $Ba(H_2O)Fe_2[PO_3(OH)]_4$, from twinned crystals, overcoming difficulties with the help of known twin laws in two related compounds, $(NH_4)In[PO_3(OH)]_2$ [6,7] and $Ba(H_2O)V_2[PO_3(OH)]_4$ [11]. Comparison of the real space groups of $P2_1/c$ or $P2_1$ with pseudosymmetry $C222_1$ in this system reveals that small average standard uncertainty (s.u.) of bond distances (i.e. estimated standard deviations) [12] is a useful criterion for the determination of centric or acentric space groups, especially when other criteria for twinned crystals are not effective. Accordingly, four common minerals with well-established space groups (i.e. calcite, dolomite, gypsum and quartz) have been selected to further test this new criterion. These minerals were known historically to have ambiguity in the determination of their space groups related to crystal twinning and/or enantiomorphism [1,13,14].

2. Preparation of materials and structure refinements

2.1. Hydrothermal syntheses

All compounds investigated in this paper have been prepared from hydrothermal methods. Herein, we only describe the synthesis of a new compound $Ba(H_2O)Fe_2^{III}[PO_3(OH)]_4$, which is another barium iron phosphate after $BaFe(PO_4)(OH)$ [15] and $Ba_2Fe_3H(PO_4)_2(P_2O_7)_2$ [16].

Crystals of $Ba(H_2O)Fe_2[PO_3(OH)]_4$ were synthesized from a mixture of 0.52 g $Ba(NO_3)_2$ (AR, 2 mmol), 0.8 g $FeCl_2 \cdot 4H_2O$ (AR, 4 mmol) and 4 mL H_3PO_4 (AR, 60 mmol) in the molar ratio of Ba:Fe:P = 1:2:30. All starting reagents were of analytical grade and were used without any further purification. After adding 5 mL deionized water, the mixture was transferred into a 25 mL Teflon-lined stainless-steel autoclave, then heated to and held at 190 °C for 3 days. After that, the autoclave left in the turn-off furnace was allowed to cool down to room temperature naturally. Solid products were filtered, washed with deionized water and dried in desiccators. Optical examination and powder X-ray diffraction (PXRD) analyses were used to identify the phases of the solid products. Scanning electron microscopy was used to document the crystal morphologies. Chemical compositions of selected crystals were first examined by use of an Oxford Instruments Energy Dispersive X-ray Spectrometer (EDX).

2.2. Characterizations of ICP-AES, TG, IR and magnetic susceptibility

The compositions of synthetic $Ba(H_2O)Fe_2[PO_3(OH)]_4$ were also determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis, which yielded the following results at obs.(e.s.d.)/calc. wt%: Ba 20.2(3)/21.1, Fe 16.36(5)/17.16, P 18.6(2)/19.0, H 0.93(3)/0.93 with the ratio of Ba:Fe:P:H = 1.00:2:4.10:6.29. This agreement between the observed and calculated results confirms the formula determined from the single-crystal XRD data (see below).

Thermal investigations (TG/DTA) were carried out in N_2 atmosphere with heating rates of 10 °C/min up to 1000 °C (NETZSCH TG 209 F1). A sharp peak at 407 °C on the DTG curve (Fig. 1) corresponds to a weight loss of ~7.5 wt%, in agreement with the expected value (8.3 wt%) assuming a loss of 3 moles of water per formula unit (i.e. 1 mole from water in the cavities and 2 moles from the condensation of the hydroxyl groups). The decomposition product after thermal treatment at 600 °C, identified by powder X-ray diffraction, is triclinic $BaFe_2(P_2O_7)_2$, which is a new polymorph and is isotypic to the β-form of its V counterpart [17–19]. Fourier transform infrared (FT-IR) spectrum further confirms the presence of hydroxyl group (3537 cm^{-1}) and water molecules (3445, 1626 cm^{-1}) (Fig. 2).

The magnetization measurements were performed on a SQUID-magnetometer (Quantum Design, MPMS XL-7) in the temperature range of 1.8–400 K using various external magnetic fields (Fig. 3). The effective paramagnetic moment μ_{eff} was calculated by linear Curie–Weiss fits $\chi(T) = C/(T - \theta)$ in the temperature range 80–400 K of the $H_{ext} = 10$ kOe data to 5.90 μ_B/Fe-atom ($\theta_p = -60.8$ K), which is consistent with the magnetic moments for Fe^{3+} in octahedral coordination. There is a hump in the $\chi(T)$ curve around 23.5(5) K

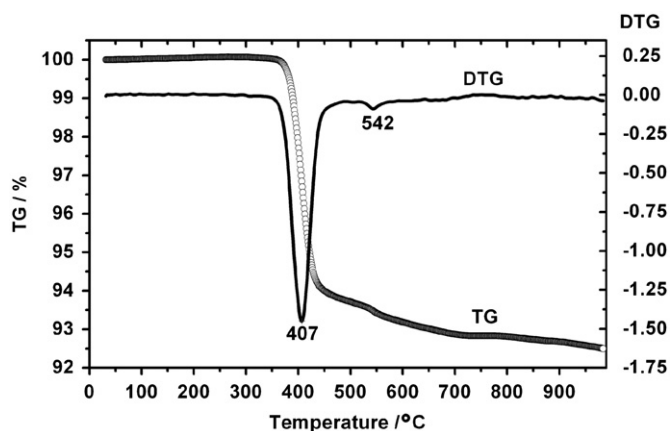**Fig. 1.** TG and DTG curves of $Ba(H_2O)Fe_2[PO_3(OH)]_4$.
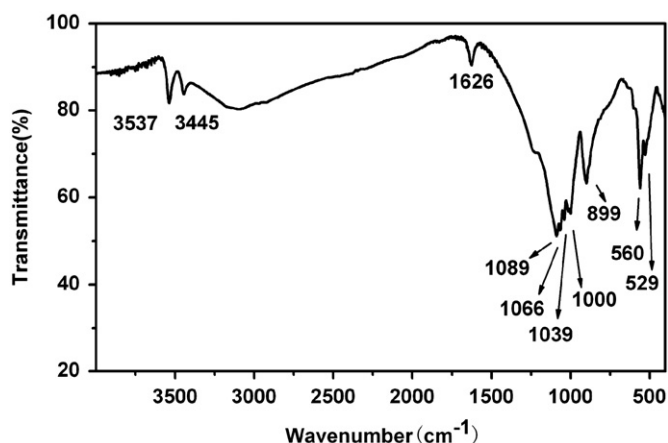
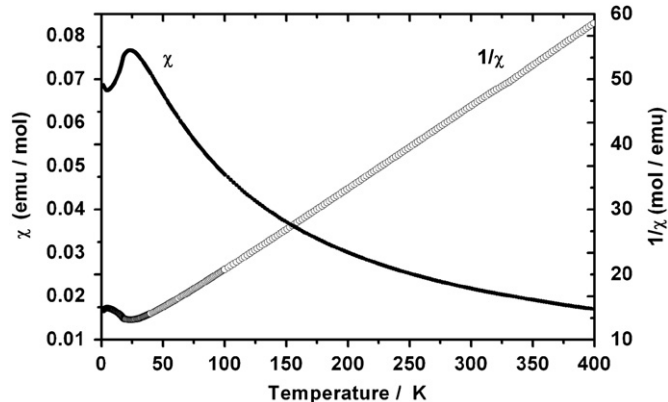**Fig. 2.** Fourier transform infrared (FT-IR) spectrum of $Ba(H_2O)Fe_2[PO_3(OH)]_4$.

Fig. 3. Temperature dependence of the molar magnetic susceptibility (χ) and inverse molar magnetic susceptibility ($1/\chi$) of $Ba(H_2O)Fe_2[PO_3(OH)]_4$.

indicating low-dimensional or frustrating interactions (Fig. 3). In addition, an antiferromagnetic long-range ordering is also observed at 17.3(1) K (Fig. 3).

2.3. Structure determinations of twinned $Ba(H_2O)M_2^{III}[PO_3(OH)]_4$ (M=Fe, V)

Synthetic crystals of $Ba(H_2O)Fe_2[PO_3(OH)]_4$ are of a single phase but exhibit two different morphologies: bipyramid and irregular form. Both types of crystals have been used to collect the single-crystal X-ray diffraction data at 173(2) K by using a Bruker

AXS SMART CCD diffractometer (Mo$K\alpha$ radiation, 50 kV/40 mA, graphite monochromator). Data collections were carried out by ω scanning with a step size of 0.3° and an exposure time of 20 s per frame. Three groups with total 1800 frames (or 1200 frames) were collected at $\chi=54.74°$, $\varphi=0$, 90 and 180°, respectively, with the crystal–detector distance of 5.948 cm.

The crystal structures were solved by direct methods and refined by the full-matrix least-squares method using the SHELXS-97 and SHELXL-97 software package [20]. Initially data reduction indicated that the crystals crystallize in a C-centered orthorhombic cell, but crystal structure analysis failed.

This situation reminded us a similar case in the crystal structure determination of $(NH_4)In[PO_3(OH)]_2$. A new batch of crystals exhibiting high optical transparency and clarity in this system was selected to collect the single crystal data on an Oxford Gemini S Ultra X-ray CCD diffractometer equipped with graphite-monochromator Mo$K\alpha$ radiation at 173 K. This single-crystal X-ray diffraction dataset yielded an orthorhombic cell with parameters: $a=10.1850(6)$ Å, $b=16.3055(9)$ Å, $c=8.2358(6)$ Å, $V=1367.74$ Å^3, and space group $C222_1$ (reflection conditions: in hkl, $h+k=2n$; in $0kl$, $k=2n$; in $h0l$, $h=2n$; in $hk0$, $h+k=2n$; in $h00$, $h=2n$; in $0k0$, $k=2n$; in $00l$, $l=2n$) (ESI Tables 1 and 2 and ESI Fig. 1). A search in the ICSD did not yield any match. Subsequently, the crystal structure was solved and refined in this orthorhombic space group by use of Shelxl-97 [20]. Table 1 shows that, besides high difference Fourier residuals (and also unexpected disorder of more than halves of atoms), the R_1 and wR_2 values are generally acceptable. However, the formula obtained from the structural analysis is the same as that reported by Mao et al. [6] and Filaretov et al. [7], except that the cell volume from the orthorhombic space group is twice of those in the monoclinic cells. Subsequently, the orthorhombic cell was transformed to a monoclinic one by a matrix $\mathbf{P}=(0.5, -0.5, 0/0, 0, -1/0.5, 0.5, 0)$. The transformed cell parameters of $a=9.6125(5)$ Å, $b=8.2358(6)$ Å, $c=9.6125(5)$ Å, $\beta=116.019°$, $V=683.86$ Å^3 are similar to those reported by Mao et al. [6] and Filaretov et al. [7]. At this point, the indices of the X-ray diffraction data were transformed by the same matrix above, using $h=(h'-k')/2$, $k=-l'$, $l=(h'+k')/2$, where h', k' and l' denote the indices in the orthorhombic setting. Due to the pseudo "reflection conditions" of $C222_1$ arising from twinning of a monoclinic cell, the index of every spot can be transformed properly into the new monoclinic setting ($P2_1$), and vice versa (ESI Fig. 1) [9]. The structure was solved by the space group $P2_1/c$ as in previous studies [6,7] and refined to $R_1=0.0170$ and $wR_2=0.0392$ by using a twin mode with a twin matrix $\mathbf{P}=(0, 0, 1/0, -1, 0/1, 0, 0)$, $k_2=0.4980(8)$ (without using the twin mode given $R_1=0.1688$, $wR_2=0.3939$). And this refinement leads to particularly good results, i.e. not only low R values but no disorder, normal weight, a clean residual density map, and significantly smaller standard uncertainty of bond distances (see below). Furthermore the transformed dataset was tentatively used for structure refinements in three other monoclinic space groups: $P2_1/c$, $P2_1/a$ and $P2_1$, all of which converged to acceptable R_1 and wR_2 values (Table 1). It is noteworthy that the present refinements in space groups $P2_1/c$ and $P2_1/a$ from a twinned crystal (Table 1) yielded R_1 and wR_2 values comparable to, even somewhat better than those from the single crystals reported by Mao et al. [6] and Filaretov et al. [7].

By taking into account of possible crystal twinning in the related compound $(NH_4)In[PO_3(OH)]_2$, the structures of the title compounds were successfully solved by the routine described above. Therefore, crystals of $Ba(H_2O)Fe_2[PO_3(OH)]_4$ are also twinned by pseudomerohedry and have a monoclinic cell with almost equal a- and c-axis ($a=9.4956(16)$ Å, $b=7.8990(14)$ Å, $c=9.4444(16)$ Å, $\beta=117.498(3)°$, $V=628.36(19)$ Å^3, space group $P2_1/c$). It gave $R_1=0.0369$ and $wR_2=0.0973$ by using the twin

Table 2
Crystal data and structure refinements of Ba(H$_2$O)M_2^{III}[PO$_3$(OH)]$_4$, (M=Fe, V).

Formula sum	BaFe$_2$H$_6$O$_{17}$P$_4$ (disordered)	BaH$_6$Fe$_2$O$_{17}$P$_4$(ordered)	BaH$_6$O$_{17}$P$_4$V$_2$(disordered)
Structural formula	[Ba$_{0.5}$,(H$_2$O)$_{0.5}$]$_2$Fe$_2$[HPO$_4$]$_4$	[Ba$_{0.944}$,(H$_2$O)$_{0.056}$][Ba$_{0.056}$,(H$_2$O)$_{0.944}$] Fe$_2$[HPO$_4$]$_4$	[Ba$_{0.5}$,(H$_2$O)$_{0.5}$]$_2$V$_2$[HPO$_4$]$_4$
Syn. temp.	240 °C	190 °C	240 °C
Crystal size (mm^3)	0.15 × 0.15 × 0.15	0.22 × 0.10 × 0.08	0.15 × 0.15 × 0.05
Form, color	Dipyramid, pale pink	Dipyramid, pale pink	Cake, green
Formula weight, Z	650.97, 2	650.97, 2	641.15, 2
Twinning type	Twinning by pseudomerohedry	Racemic twin	Twinning by pseudomerohedry
Twinning matrix	(0, 0, 1/0, −1, 0/1, 0, 0)	(1, 0, 0/0, −1, 0/0, 0, 1)	(0, 0, 1/0, −1, 0/1, 0, 0)
Twin ratio K$_2$, Ba/H$_2$O	0.395(2), disorder	0.466(17), partial order	0.445(2), disorder
|E^2-1|, Friedel pairs	0.786, –	0.690, 1154	0.741, -
Ba1/Ow1, Ba2/Ow2	50% /50%, −/−	94.4(2)%/5.6%, 5.6%/94.4%	50% /50%, −/−
Crystal sys., S.G.	Monoclinic, P2$_1$/c	Monoclinic, P2$_1$(No.4)	Monoclinic, P2$_1$/c
Cell parameters(Å, °, Å^3)	a=9.4956(16), b=7.8990(14), c=9.4444(16), β=117.498(3), V=628.36(19)	a=9.478(2), b=7.9213(19), c=9.396(2), β=117.392(4), V=626.4(3)	a=9.4740(16), b=7.9031(13), c=9.4592(16), β=117.636(3), V=627.45(18)
Rad. (Å), temp. (K)	0.71073, 173(2)	0.71073, 173(2)	0.71073, 173(2)
μ (mm^{-1}), F(000)	5.992, 620	6.011, 620	5.179, 608
$2\theta_{max}$(°), Dcalc.	56.62, 3.441	56.94, 3.452	56.28, 3.394
Miller-index	−12 ≤ h ≤ 12, −10 ≤ k ≤ 10, −12 ≤ l ≤ 12	−12 ≤ h ≤ 6, −9 ≤ k ≤ 10, −11 ≤ l ≤ 12	−12 ≤ h ≤ 12, −10 ≤ k ≤ 10, −12 ≤ l ≤ 12
R_{int}, $R_{\sigma(1)}$	0.0387, 0.0387	0.0169, 0.0327	0.0321, 0.0333
S, Wa, Wb	1.002, 0.0643, 2.4220	1.000, 0.0406, 0.9256	1.000, 0.0793, 5.0795
R_1, wR_2	0.0369, 0.0973	0.0238, 0.0642	0.0422, 0.1201
N_{all}(N_{gt}), N_{para}	1530 (1521) , 111	2664 (2640), 230	1507 (1488),112
LDPH^i, Pearson	1.689, −1.073, mP60	1.020, −0.601, mP60	1.192, −1.047, mP60
ASUBD^{ii}	σ(Fe–O)=0.0037 σ(P–O)=0.0037	σ(Fe−O)=0.0037 σ(P−O)=0.0039	σ(V−O)=0.0051 σ(P−O)=0.0051

(i) and (ii) abbreviations of LDPH and ASUBD are same as in Table 1.

Table 3
Atomic coordinates and isotropic atomic displacement parameters of disordered Ba(H$_2$O)Fe$_2$[PO$_3$(OH)]$_4$ in space group P2$_1$/c.

Atom	Occupancy	x/a	y/b	z/c	U (Å^2)
Ba(1)/OW(1)^a	0.5/0.5	0.85371(7)	0.37778(8)	0.42129(7)	0.01692(18)
Fe(1)	1.0	0.25421(8)	0.11677(9)	0.48780(8)	0.00722(18)
P(1)	1.0	0.09017(15)	0.06632(15)	0.72829(15)	0.0071(3)
P(2)	1.0	0.48297(16)	0.18629(15)	0.32131(16)	0.0076(3)
O(1)	1.0	0.1245(5)	0.1463(5)	0.6020(5)	0.0151(8)
O(2)	1.0	0.1478(5)	0.1723(5)	0.8786(5)	0.0137(8)
O(3)	1.0	0.3580(4)	0.0856(4)	0.3458(4)	0.0089(7)
O(4)	1.0	0.6411(4)	0.0909(5)	0.3831(5)	0.0118(7)
O(5)	1.0	0.9122(5)	0.4661(5)	0.1664(5)	0.0150(8)
O(6)	1.0	0.4311(4)	0.2370(5)	0.1481(4)	0.0106(7)
O(7)	1.0	0.5185(5)	0.3581(5)	0.4180(4)	0.0144(8)
O(8)	1.0	0.8230(5)	0.1084(4)	0.2238(5)	0.0172(8)
H(1)	1.0	0.4674	0.3647	0.4736	0.04(3)
H(2)	1.0	0.7346	0.1531	0.1435	0.05

^{a} Barium atoms and water molecules are located at the same sites within the cavities.

mode with a twin matrix $\boldsymbol{P}$=(0, 0, 1/0, −1, 0/1, 0, 0), k_2=0.395(2), in comparison with R_1=0.1858 and wR_2=0.4953 without the twinned mode. The ADDSYM routine of PLATON [21] does not indicate the presence of orthorhombic symmetry, although the cell parameters can be transformed to a pseudo-orthorhombic lattice. Barium and water molecules are located at the same site with 50% population each in the cavities.

In an attempt to obtain a 'real' single crystal without twinning for structure refinement, we collected X-ray diffraction datasets on more than 10 crystals. No single crystal was found. However, structure refinements of these datasets led us to discover that the degree of order for the barium cations and water molecules in the cavities varies among the crystals investigated, from a completely disordered variety (Ba$_{0.5}$,(H$_2$O)$_{0.5}$) to those with partial ordering such as (Ba(1)$_{0.67}$,(H$_2$O)$_{0.33}$)/(Ba(2)$_{0.33}$,(H$_2$O)$_{0.67}$) to an almost

completely ordered type (Ba(1)$_{0.94}$,(H$_2$O)$_{0.06}$)/(Ba(2)$_{0.06}$,(H$_2$O)$_{0.94}$). The ordered or partially ordered varieties have an acentric space group P2$_1$. One of the datasets with an almost completely ordered structure, for which the structure could not be solved in centric space group P2$_1$/c, is given in Table 2. Here, an anisotropic refinement of the structure in P2$_1$, by using different occupancies of Ba (and H$_2$O) (i.e. two crystallographic sites split from one position in P2$_1$/c), converged to R_1=0.0238 and wR_2=0.0642, using a twin mode with a twin matrix $\boldsymbol{P}$=(1, 0, 0/0, −1, 0/0, 0, 1), k_2=0.466(17) (without using the twin mode: R_1=0.0273 and wR_2=0.0734). These results show that the centrosymmetry P2$_1$/c in this case is broken only by the ordering of Ba (and H$_2$O) atoms in the cavities. ADDSYM finds 100% fit for coordinates between the centric and acentric space groups, except for Ba (and H$_2$O) occupancies. Therefore, the ADDSYM routine of PLATON [21] is

not useful in this particular case. Also, these ordered crystals possess another type of twinning: i.e. twinning by merohedry (racemic twin).

It is also interesting to note that the related compound, $Ba(H_2O)V_2[PO_3(OH)]_4$, was originally reported in the acentric space group $P2_1$ [11]. In order to determine the distribution of barium and water molecules in this vanadium analog, we synthesized crystals of $Ba(H_2O)V_2[PO_3(OH)]_4$. Structure determinations demonstrate that these crystals are also twinned with a pseudo-orthorhombic cell. The procedure above applied in our structure refinement of synthetic $Ba(H_2O)Fe_2[PO_3(OH)]_4$ was also straight forward. The crystal structure of $Ba(H_2O)V_2[PO_3(OH)]_4$ in

$P2_1/c$ was refined to $R_1=0.0422$ and $wR_2=0.1201$ by using a twin matrix $\boldsymbol{P}=(0, 0, 1/0, -1, 0/1, 0, 0)$, $k_2=0.395(2)$, in comparison with $R_1=0.2106$ and $wR_2=0.5057$ without the twin mode. Therefore, our synthetic $Ba(H_2O)V_2[PO_3(OH)]_4$ possesses space group $P2_1/c$ with a disordered distribution of Ba and H_2O, in comparison with the acentric $P2_1$ variety reported by Wang et al. [11].

The atomic coordinates and isotropic atomic displacement parameters, anisotropic atomic displacement parameters, as well as selected interatomic distances and angles of the disordered compounds $(P2_1/c)$ $Ba(H_2O)M_2^{III}[PO_3(OH)]_4$ (M=Fe, V) are given in Tables 2–7. Further details of these crystal structure

Table 4
Anisotropic atomic displacement parameters (in Å²) of disordered $Ba(H_2O)Fe_2[PO_3(OH)]_4$ in space group $P2_1/c$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ba(1)/OW(1)	0.0185(3)	0.0182(3)	0.0192(3)	0.0018(2)	0.0131(3)	0.0020(2)
Fe(1)	0.0067(4)	0.0060(3)	0.0105(4)	−0.0002(3)	0.0053(3)	0.0000(3)
P(1)	0.0070(6)	0.0051(5)	0.0101(6)	−0.0004(4)	0.0048(5)	−0.0004(4)
P(2)	0.0071(6)	0.0057(5)	0.0118(6)	0.0014(4)	0.0059(5)	0.0019(5)
O(1)	0.020(2)	0.0151(18)	0.018(2)	−0.0015(15)	0.0154(18)	0.0013(16)
O(2)	0.0160(19)	0.0141(17)	0.0146(19)	−0.0060(15)	0.0102(16)	−0.0044(15)
O(3)	0.0101(16)	0.0059(15)	0.0106(18)	−0.0023(14)	0.0047(14)	−0.0015(13)
O(4)	0.0084(17)	0.0097(15)	0.0190(19)	0.0012(14)	0.0078(15)	0.0034(15)
O(5)	0.0084(17)	0.0175(18)	0.021(2)	0.0067(15)	0.0086(16)	0.0092(16)
O(6)	0.0117(17)	0.0094(16)	0.0122(18)	0.0047(14)	0.0070(15)	0.0023(14)
O(7)	0.0192(19)	0.0096(16)	0.0155(18)	−0.0031(14)	0.0089(15)	−0.0033(15)
O(8)	0.0168(16)	0.0078(15)	0.0198(17)	0.0055(14)	0.0023(13)	0.0008(13)

Table 5
Atomic coordinates and isotropic atomic displacement parameters of disordered $Ba(H_2O)V_2[PO_3(OH)]_4$ in space group $P2_1/c$.

Atom	Occupancy	x/a	y/b	z/c	U (Å²)
Ba(1)/OW(1) [a]	0.5/0.5	0.85497(10)	0.38145(11)	0.42135(10)	0.0158(2)
V(1)	1.0	0.25459(12)	0.11477(15)	0.48791(12)	0.0045 (2)
P(1)	1.0	0.0899(2)	0.0666(2)	0.7283(2)	0.0068 (3)
P(2)	1.0	0.4849(2)	0.1859(2)	0.3217(2)	0.0073 (3)
O(1)	1.0	0.1226(7)	0.1455(7)	0.6021(7)	0.0155(11)
O(2)	1.0	0.1481(7)	0.1730(7)	0.8796(6)	0.0149(11)
O(3)	1.0	0.3584(6)	0.0835(6)	0.3448(6)	0.0095(10)
O(4)	1.0	0.6421(6)	0.0913(7)	0.3831(6)	0.0120(10)
O(5)	1.0	0.9136(6)	0.4707(7)	0.1705(7)	0.0139(11)
O(6)	1.0	0.4333(6)	0.2392(6)	0.1474(5)	0.0072 (9)
O(7)	1.0	0.5183(6)	0.3584(7)	0.4180(6)	0.0138(10)
O(8)	1.0	0.8201(6)	0.1094(6)	0.2221(6)	0.0175(11)
H(1)	1.0	0.4674	0.3647	0.4736	0.04(3)
H(2)	1.0	0.7346	0.1531	0.1435	0.0500

[a] Barium atoms and water molecules are situated together within the cavities.

Table 6
Anisotropic atomic displacement parameters (in Å²) of disordered $Ba(H_2O)V_2[PO_3(OH)]_4$ in space group $P2_1/c$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ba(1)/OW(1)	0.0180(4)	0.0184(4)	0.0156(4)	0.0041(3)	0.0118(3)	0.0039(3)
V(1)	0.0037(5)	0.0051(5)	0.0056(5)	0.0003(4)	0.0028(4)	−0.0005(4)
P(1)	0.0067(8)	0.0075(7)	0.0074(8)	−0.0011(6)	0.0042(6)	0.0004(6)
P(2)	0.0076(8)	0.0085(8)	0.0077(8)	0.0005(6)	0.0050(6)	0.0022(6)
O(1)	0.018(2)	0.018(2)	0.017(2)	−0.0032(17)	0.0138(18)	0.0030(17)
O(2)	0.019(3)	0.017(3)	0.015(3)	−0.011(2)	0.013(2)	−0.008(2)
O(3)	0.012(2)	0.008(2)	0.006(2)	−0.0011(18)	0.0020(18)	−0.0040(16)
O(4)	0.010(2)	0.012(2)	0.017(2)	−0.001(2)	0.008(2)	0.004(2)
O(5)	0.009(2)	0.021(3)	0.016(3)	0.004(2)	0.009(2)	0.004(2)
O(6)	0.011(2)	0.007(2)	0.006(2)	0.0039(18)	0.0058(19)	0.0017(18)
O(7)	0.016(2)	0.014(2)	0.012(2)	−0.005(2)	0.007(2)	−0.005(2)
O(8)	0.015(3)	0.009(2)	0.022(2)	0.006(2)	0.0027(19)	0.001(2)

Table 7
Selected bond distances (in Å) and bond valence sum (BVS) of disordered Ba(H$_2$O)Fe$_2$[PO$_3$(OH)]$_4$ and Ba(H$_2$O)V$_2$[PO$_3$(OH)]$_4$ in space group $P2_1/c$.

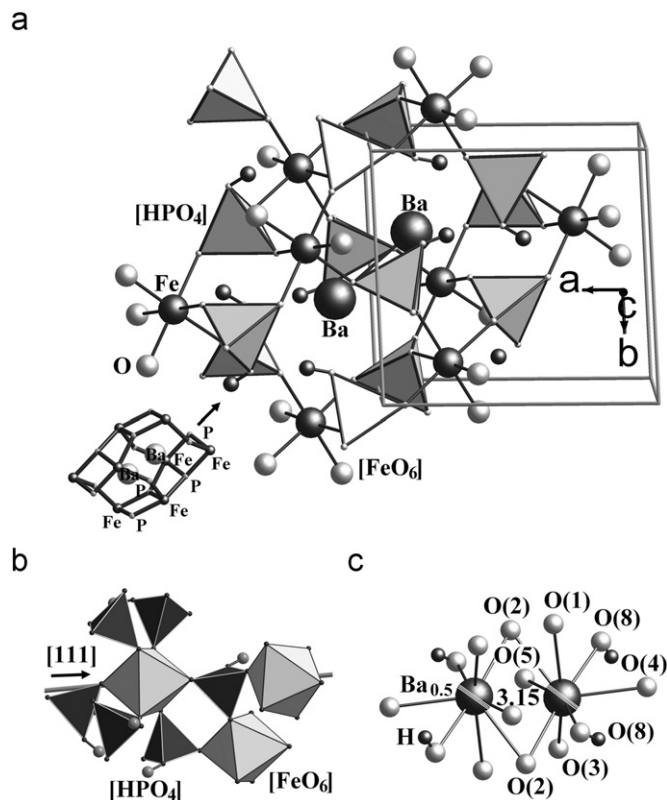| Ba(H$_2$O)Fe$_2$[PO$_3$(OH)]$_4$	Ba(H$_2$O)V$_2$[PO$_3$(OH)]$_4$
Ba(1)–O(8) 2.755(4)	Ba(1)–O(8) 2.776(5)
O(5) 2.797(4)	O(5) 2.767(5)
O(3) 2.901(4)	O(3) 2.873(5)
O(4) 2.944(4)	O(4) 2.963(5)
O(1) 2.969(4)	O(1) 2.968(6)
O(2) 3.002(4)	O(2) 2.984(5)
O(8) 3.005(4)	O(8) 3.013(6)
O(2) 3.027(4)	O(2) 3.012(5)
O(7) 3.172(4)	O(7) 3.180(5)
Mean, BVS: 2.953, 1.580[a]	Mean, BVS: 2.949, 1.600[a]
Fe(1)–O(2) 1.974(4)	V(1)–O(2) 1.980(5)
O(5) 1.978(4)	O(5) 1.966(5)
O(1) 1.991(3)	O(1) 2.011(5)
O(4) 2.012(4)	O(4) 1.998(5)
O(3) 2.013(3)	O(3) 2.024(5)
O(6) 2.025(4)	O(6) 2.026(5)
Mean, BVS: 1.999, 3.143	Mean, BVS: 2.000, 2.998
P(1)–O(1) 1.512(4)	P(1)–O(1) 1.502(5)
O(2) 1.516(4)	O(2) 1.525(5)
O(5) 1.533(4)	O(5) 1.526(5)
O(8) 1.564(4)	O(8) 1.585(5)
Mean, BVS: 1.531, 4.879	Mean, BVS: 1.535, 4.841
P(2)–O(6) 1.528(4)	P(2)–O(6) 1.545(5)
O(3) 1.532(4)	O(3) 1.543(5)
O(4) 1.534(4)	O(4) 1.521(5)
O(7) 1.583(4)	O(7) 1.588(5)
Mean, BVS: 1.544, 4.710	Mean, BVS: 1.549, 4.646
Ba(1)–Ba(1) 3.1374(13)	Ba(1)–Ba(1) 3.0795 (18)
O–Fe–O: 83.62 (0.16)–94.65 (0.18)	O–V–O: 83.2(2)–93.3(2)
O–P(1)–O: 107.6(2)–113.0(2)	O–P(1)–O: 106.6(3)–113.5(3)
O–P(2)–O: 105.7(2)–114.1(2)	O–P(2)–O: 105.0(3)–114.3(3)

[a] Affected by barium atoms and water molecules situated together within the cavities.

Fig. 4. Crystal structure of Ba(H$_2$O)Fe$_2$[PO$_3$(OH)]$_4$: (a) inset in the left shows pairs of triple squares of [FeO$_6$] and [HPO$_4$]; (b) the connection motif of [FeO$_6$] and [HPO$_4$]; and (c) coordination environments of Ba with 50% occupancies [Ba$_{0.5}$, (H$_2$O)$_{0.5}$].

3. Results and discussion

3.1. Description of the crystal structures

The crystal structures of Ba(H$_2$O)M_2^{III}[PO$_3$(OH)]$_4$ (M=Fe, V) are isotypic to that of (NH$_4$)In[PO$_3$(OH)]$_2$. These structures are characterized by [MO$_6$] octahedra sharing O-corners with [HPO$_4$] tetrahedra to form a three-dimensional framework. Each [MO$_6$] octahedron shares all six O-corners with six different [HPO$_4$] groups, while every [HPO$_4$] tetrahedron with a terminal OH group shares three of its four O-corners with three different [MO$_6$] octahedra. Pairs of [HPO$_4$] groups bridge two [MO$_6$] octahedra to form a four-membered square net, likes a ladder, running along [111] or [1$\bar{1}$1] (Figs. 4 and 5). These paralleled ladders are linked together via [HPO$_4$] groups, whereas the cross-direction ladders, along [111] or [1$\bar{1}$1], join together by [MO$_6$] octahedra as shown in Fig. 5. All ladders combining together via the aforementioned [MO$_6$] octahedra or [HPO$_4$] groups form a three dimensional framework. Barium cations and water molecules (H$_2$O) are located together in the cavities surrounded by a pair of triple squares and the bridged [HPO$_4$] groups (Fig. 4a inset). Ba(H$_2$O)M_2^{III}[PO$_3$(OH)]$_4$ (M=Fe, V) can be considered as isomorphs of (NH$_4$)In[PO$_3$(OH)]$_2$ via a substitution of 2[NH$_4$]$^+$+2In^{3+} by Ba^{2+}+H$_2$O+2Fe^{3+} (or 2V^{3+}). The effective ionic radius (r=1.61 Å, CN=12) of Ba^{2+} [22] is smaller than that (r=1.729 Å, CN=12) of [NH$_4$]$^+$ [23]. Barium cations and

water molecules are located at the same site as [NH$_4$]$^+$ in (NH$_4$)In[PO$_3$(OH)]$_2$. Disordered distribution of barium and H$_2$O with 50% occupancies each gives rise to the centrosymmetric space group $P2_1/c$, whereas an ordered or partially ordered distribution yields the space group $P2_1$.

3.2. Standard uncertainty of bond distances as a sensitive criterion

It is interesting that structure refinement of the compound (NH$_4$)In[PO$_3$(OH)]$_2$ in the acentric space group $P2_1$ converged as well, yielding similar R_1 and wR_2 values and other parameters (e.g., goodness of fit and difference electron density peaks/holes) comparable to those from the centrosymmetric space groups $P2_1/c$ and $P2_1/a$ (Table 1). This result shows that these parameters are not useful for distinguishing the centrosymmetric and non-centrosymmetric space groups in this case. One notable exception is that the average standard uncertainty [σ(P–O)=0.0108 Å] of bond distances for the PO$_4$ tetrahedron in $P2_1$ is notably larger than those from the space groups $P2_1/c$ [σ(P–O)=0.0024 Å] and $P2_1/a$ [σ(P–O)=0.0023 Å]. Similarly, the average standard uncertainty of bond distances for the PO$_4$ tetrahedron in $C222_1$ [σ(P–O)= 0.0162 Å] is significantly larger than those in $P2_1/a$ and $P2_1/c$ as well (Table 1).

We hypothesize that centrosymmetry, if falsely lowered to acentric symmetries, would cause to break symmetry constraints, double the number of strongly correlated parameters and result in large uncertainties of the atomic displacement parameters as well as anomalously large uncertainties of bond distances. Similarly, falsely enhanced symmetry is expected to cause disorder of some atoms owing to symmetry restrictions as well, thus producing abnormal temperature factors and larger
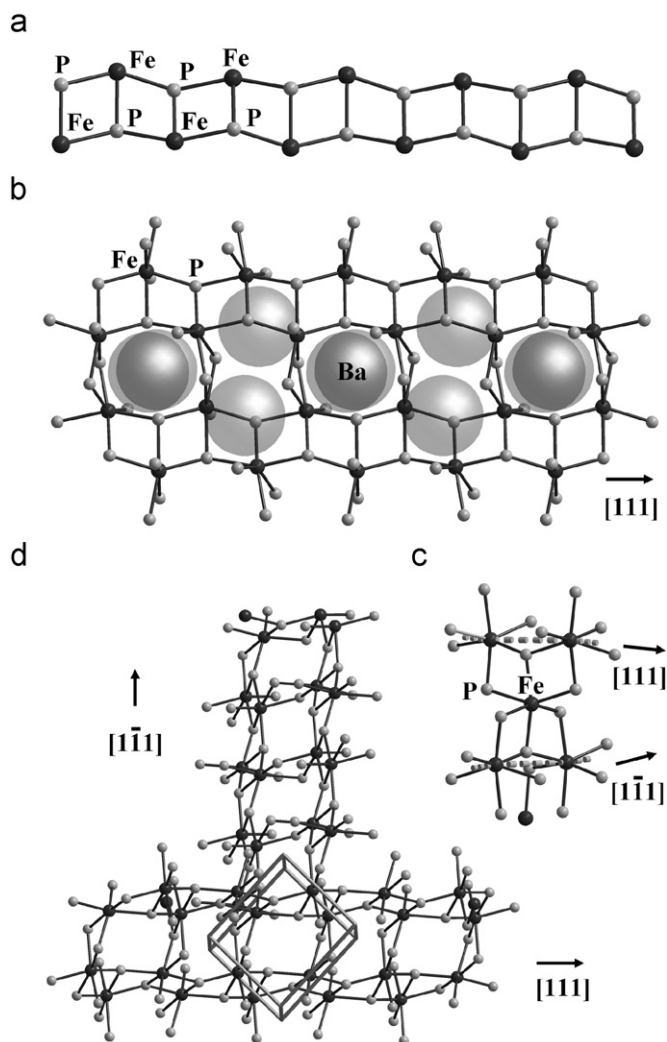
Fig. 5. Topological connectivity of the [FeO$_6$] octahedra and the [HPO$_4$] tetrahedra of Ba(H$_2$O)Fe$_2$[PO$_3$(OH)]$_4$. (a) a ladder consisting of four-membered square net of [FeO$_6$] and [HPO$_4$]; (b) a net composed of parallel ladders along [111]; (c) an octahedron of [FeO$_6$] connects the across-direction ladders along [111] and [1$\bar{1}$1]; and (d) three-dimensional framework consisting of the across-direction ladders along [111] and [1$\bar{1}$1].

standard uncertainties of bond distances. In the case of our series of order–disordered title compounds, structure refinements of the ordered compound, although it has twice as many parameters as its disordered counterpart does, yielded much smaller R values and standard uncertainties of bond distances than the centric model. Therefore, small standard uncertainties of bond distances can lead to a proper selection of space groups, and vice versa. We note that International Union of Crystallography (IUCr) does recommend standard uncertainty of bond distances as a criterion for evaluating structure refinements. Indeed, standard uncertainty of bond distances remains unreported in many crystal structure studies.

Baur and Fischer [12] noted that small deviations of bond distances could result from higher symmetries. Our results show that a falsely high symmetry only leads to small deviations of the cell parameters, not the deviation of bond distances. Indeed, only a correct choice of space group would result in small standard uncertainty of bond distances, whereas incorrect space groups (irrespective of higher or lower symmetry) cause significantly larger standard uncertainties of bond distances. Therefore, small average standard uncertainty of bond distances

is potentially a very sensitive parameter for determination of space groups.

This criterion played a decisive role in the determination of space groups for the new compound Ba(H$_2$O)Fe$_2$[PO$_3$(OH)]$_4$, as well as its vanadium counterpart. In these cases, order–disorder takes place in the occupancies of Ba and H$_2$O only. Crystal twinning resulted in wrong diffraction symbols, e.g. possible space groups of $C222_1$, $P2_1$ and $P2/m$ given in the statistical distribution of the reflection intensities for the title compounds. The criterion of mean $|E*E-1|$ is not valid for determining the inversion center and twinning for these special cases (Table 2 and ESI Tables 1 and 2). Therefore, the commonly used Bruker Xprep program and the ADDSYM routine of PLATON [21] are not useful for the choice of proper space groups in these cases. We also noticed that, while the previously reported R_1 and wR_2 values for Ba(H$_2$O)V$_2$[PO$_3$(OH)]$_4$ in $P2_1$ [11] are reasonable, its average standard uncertainties of bond distances of the VO$_6$ and PO$_4$ groups [i.e. σ(V–O)=0.012 Å and σ(P–O)=0.013 Å] are considerably larger than those [σ(V–O)=0.0051 Å and σ(P–O)=0.0051 Å] obtained in this study. Additionally, the bond valence sum (1.76) of Ba is also slightly smaller than the ideal value of $+2$ [24]. It is possible that the structure refinement in [11] had unresolved problems. Indeed, we note that the isotropic atomic displacement parameter for Ba in [11] is three times larger than those for V and P, and is also larger than those for most of the oxygen atoms. This anomalous value suggests that the Ba position could be partially substituted by water molecules, as observed in the iron counterparts. By contrast, the standard uncertainties of the atomic displacement parameters of the Fe counterparts in ordered or partially ordered structures with a space group of $P2_1$ have comparably small values as those from the centric space group ($P2_1/c$) of the disorder compound. We emphasize that the standard uncertainties of the atomic displacement parameters closely correlate with the atomic weights of individual elements. A proper structure determination would lead to small standard uncertainties of the atomic displacement parameters as well as small standard uncertainties of bond distances. Therefore, these examples demonstrate that the average standard uncertainty of bond distances is more sensitive than most of the conventional criteria proposed for structure determination. More specifically, we suggest that any crystal structures with standard uncertainties of bond distances over 0.01 Å, if not from poor crystal quality, should be re-examined.

Indeed, determination of space groups has always been a challenge in crystallography. In many cases, space group is not uniquely determined by X-ray reflection conditions owing to Friedel's rule. In other words, diffraction patterns always include an inversion center, which may not be present in the crystal [25]. Often when anomalous dispersion is taken into account, differences between reflections hkl and $\bar{h}\bar{k}\bar{l}$ can help us to determine whether an inversion center exists in the crystal or not. However, determination of enantiomorphic space groups is commonly ambiguous. As pointed out by Looijenga-Vos and Buerger [25], other causes of difficulty in space group determinations include, but are not limited to (1) crystal twinning, (2) incorrect determination of reflection conditions and (3) incorrect assignment of the Laue symmetry. Consequently, the space groups reported for many compounds in the literature are doubtful and ambiguous. For example, Marsh and Clemente [26] claimed revisions of 188 compounds' space groups published in the Journal of the American Chemical Society, while Clemente and Marzotto [27], Herbstein et al. [28] and Baur and Kassner [29] gave additional examples from other journals and databases. Clemente and Marzotto [27] claimed that "approximately 800 structures" with space groups of "unnecessarily low symmetry" had been revised and "nearly 7000 incorrect structures" might be included in the

Cambridge Structural Database (CSD) before November 2002. Marsh [30] and his colleagues in their series of work claimed thousands of compounds reported with unnecessary low symmetries. Reported structures in the Cambridge Structural Database described in space groups of inappropriately low symmetry have occupied the percentage close to 5% out of space group Cc and 8% out of space group $P1$ [30]. Implementation of computer programs such as PLATON [21] has helped crystallographers to avoid most of these problems, and the number of false space groups reported has steadily declined from $\sim 3\%$ [31] to 0.5–1.0% [26]. A large number of false monoclinic cells have been evaluated and transformed to C-centered orthorhombic cells, for example Clemente and Marzotto [27] reported 10 cases of this type out of 30 examples investigated. In contrast, few cases of real monoclinic cells that appear to have pseudo-orthorhombic C-centered cells have been reported [9,10].

Determination of space groups in some cases remains a real problem. We note that re-evaluations of space groups in the literature are based on various criteria, which are sometimes arbitrary and may not work in specific cases. Therefore, a general and widely applicable criterion for determination of space groups, such as the small average standard uncertainty of bond distances, is particularly desirable.

In this context, our structure refinements of synthetic calcite, dolomite, gypsum and quartz (ESI Tables 3 and 4) provide an opportunity to further optimize this criterion based on the small average standard uncertainty of bond distances. All structure refinements of these common minerals used both centric and acentric space groups, yielding comparable R_1 and wR_2 values. However, correct space groups are clearly indicated by small average standard uncertainty of bond distances in all four cases (ESI Tables 3 and 4) [13,32–35].

These results, therefore, provide further evidence that small standard uncertainty of bond distances is a sensitive criterion for determination of space groups. The merit of this criterion is particularly evident in these selected examples where other commonly used parameters such as R_1 and wR_2 values are not useful.

4. Conclusion

In summary, determination of space groups remains a significant challenge in crystallography. Development and application of various computer programs have helped to avoid most of the possible pitfalls, but problems in special cases persist. This present study demonstrates that small average standard uncertainty of bond distances is an extremely sensitive criterion for determination of space groups. By using this criterion, we have successfully determined the crystal structures of a novel series of order–disorder species $Ba(H_2O)Fe_2[PO_3(OH)]_4$ from twinned crystals with a pseudo-orthorhombic cell ($C222_1$), and found that previous refinement of their vanadium counterpart [8] may be problematic. In particular, we suggest that this criterion should be included routinely in the studies of twinned crystals, as well as order–disorder crystals, which are increasingly used in structure refinements.

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2011.12.043.

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