of 436 K. Therefore, the value measured on heating alone shows a difference of 13 K as compared with the corresponding mean value. If this misfit is transferred to the observed peak at 359 K, a corrected transition temperature of 346 (10) K results.

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Structural Instabilities of the Trigonally Coordinated Water Molecules in Ba(IO₃)₂.H₂O and Pb(ClO₃)₂.H₂O Studied by X-ray and Neutron Diffraction at 25 and 295 K

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Abstract

Structural parameters are given for the isotypic title compounds, both monoclinic, $I2/c$, $Z = 4$. Barium diiodate monohydrate, Ba(IO₃)₂.H₂O: $M_r = 505.16$, $T_1 = 295$ K, neutron data, $R = 0.0359$ for 559 observed unique reflections; $T_2 = 25$ K, X-ray data, $R = 0.0291$ (2327 reflections). Lead dichlorate monohydrate, Pb(ClO₃)₂.H₂O: $M_r = 392.11$, $T_1 = 295$ K, neutron data, $R = 0.0296$ (480 reflections) and 0.0351 (466 reflections) for two independent investigations on different crystals; $T_2 = 25$ K, neutron data, $R = 0.0302$ (755 reflections). An inter-experimental comparison indicates that the room-temperature neutron data for Pb(ClO₃)₂.H₂O are largely free of systematic errors, notably extinction effects. At room temperature the water molecules in both compounds exhibit

Table 1. *Crystallographic data and experimental and refinement parameters*

	$Ba(IO_3)_2.H_2O$		Crystal (I)	$Pb(ClO_3)_2.H_2O$ Crystal (II)	
Temperature (K)	295	25	295	295	25
Method	Neutron	X-ray		Neutron	Neutron
Instrument used	D19, ILL Grenoble	Huber/Aracor four-circle		SV28, KFA Jülich	R2 Studsvik
λ (Å)	1.270	0.7107		1.238	1.215
$F(000)$	195.85 fm	880		246.79 fm	246.79 fm
Lattice parameters a (Å)	9.048 (1)	9.022 (5)		8.811 (1)	8.755 (1)
b (Å)	7.987 (2)	7.937 (4)		7.744 (1)	7.697 (1)
c (Å)	9.911 (1)	9.867 (6)		9.131 (1)	9.130 (1)
β (°)	92.13 (1)	92.18 (5)		93.13 (1)	93.45 (1)
Unit-cell volume V (Å³)	715.7 (1)	706.0 (5)		622.1 (1)	614.1 (1)
D_x (Mg m⁻³)	4.69	4.75		4.19	4.24
μ(calc) (cm⁻¹)	0.067	143.5		0.131	0.133
No. of reflections used for lattice-parameter determination	(a)	34		(a)	15
2θ range (°)	–	25–30		–	20–70
Crystal size (mm)	1.02 × 0.54 × 0.34	0.09 × 0.08 × 0.04	8.1 × 4.6 × 3.9	4.5 × 2.9 × 1.5	6.4 × 2.2 × 1.0
Max./min. absorption correction (numerical integration)	Not applied	0.594/0.325	0.954/0.936	0.982/0.964	0.988/0.964
Measured range of 2θ (°)	2–90	2–90	3–90	3–90	3–107
$[(\sin\theta)/\lambda]_{max}$ (Å⁻¹)	0.63	0.995	0.57	0.57	0.66
Range of h, k, l measured	−10→10, 0→9, 0→12	−17→0, −15→15, −19→19	−10→10, 0→8, −10→10	−10→10, 0→8, 0→10	−12→12, −10→0, 0→12
No. of standard reflections	2	5	1	1	3
Timewise variation	Insignificant	−2.4%, linear correction	Insignificant	Insignificant	Insignificant
No. of measured reflections	797	5334	1488	575	939
Limit for observed reflections	$2.0\sigma(F^2)$	$2.0\sigma(F^2)$	$0.5\sigma(F^2)$	$0.5\sigma(F^2)$	$2.0\sigma(F^2)$
Observed unique reflections	559	2308	480	466	739
No. of refined parameters	57	52	57	57	62
R_{int}	0.014[b]	0.0284	0.0086	0.0119[b]	0.0059[b]
Extinction coefficient	7.3 (3) × 10⁻⁷	3.9 (3) × 10⁻⁷	3.9 (1) × 10⁻⁶	2.33 (9) × 10⁻⁷	(c)
k in weighting scheme	0.024	0.020	0.005	0.008	0.030
Max./min. $\Delta\rho$	0.41/−0.36 fm Å⁻³	4.4/−3.5 e Å⁻³	0.44/−0.45 fm Å⁻³	0.49/−0.45 fm Å⁻³	0.64/−0.58 fm Å⁻³
R	0.0359	0.0275	0.0296	0.0351	0.0302
wR	0.0362	0.0448	0.0252	0.0270	0.0442
S	0.94	1.96	1.45	0.96	1.07

Notes: (a) Lattice parameters at 295 K from X-ray powder data, Guinier IV technique, Cr $K\alpha_1$ radiation, α-quartz as internal standard (Lutz, Alici & Buchmeier, 1986). Lattice parameters at 25 K from diffractometer data. (b) R_{int} indicates in these cases mainly the agreement of the check reflections (owing to beam-time limitations, only one asymmetric unit was measured). (c) Anisotropic model according to Becker & Coppens (1974, 1975), Lorentzian mosaic spread distribution, anisotropy of mosaic spread according to Thornley & Nelmes (1974). Numerical values of the refined coefficients: 0.31 (6) × 10⁴, 0.45 (9) × 10⁴, 0.13 (2) × 10⁴, −0.33 (6) × 10⁴, 0.8 (3) × 10³, −0.9 (5) × 10³.

a similar dynamic disorder as shown by the large anisotropy of the thermal ellipsoids of the O atoms and by vibrational spectroscopy. At low temperatures the behaviour is different: a single-minimum position with normal displacement parameters is found for $Pb(ClO_3)_2.H_2O$, whereas $Ba(IO_3)_2.H_2O$ exhibits a double-minimum position for the water O atom. These strikingly different ordering modes in two otherwise very similar compounds are a result of the different metal–oxygen bond strengths, which are also revealed from double matrix-isolation vibrational spectra. Hydrogen bonding seems to have very little effect on the overall structure.

Introduction

It has been found from room-temperature single-crystal X-ray studies for all seven known compounds of the $M(XO_3)_2.H_2O$ type (M = Ba, Sr, Pb; X = Cl, Br, I) that the displacement parameters of the water O atom exhibit a pronounced elongation normal to the HOH plane (Kartha, 1952a,b; Manotti Lanfredi, Pellinghelli, Tiripicchio & Tiripicchio Camellini, 1972; Lutz, Alici & Buchmeier, 1986). However, structure refinements for $Sr(IO_3)_2.H_2O$ (Lutz, Kellersohn & Vogt, 1990) and $Sr(BrO_3)_2.H_2O$

(Kellersohn, Lutz, Gonschorek & Weitzel, 1990) based on 295 K single-crystal neutron data gave no evidence of statistical disorder of the water molecule. It was therefore concluded that this structural instability is entirely dynamic at room temperature, a view supported by the temperature dependence of the half-widths of the OH (OD) stretching bands in both IR and Raman spectra (Lutz & Lange, 1990). The spectra also indicate that the dynamic behaviour freezes in the range 131–187 K for all compounds. On the other hand, no indications of a structural phase transition were observed by DSC or X-ray powder diffraction down to 100 K.

The purpose of the present investigations was therefore twofold: first, to obtain precise hydrogen-bond parameters in connection with our previous studies on this structure type, since neutron diffraction studies on the title compounds have not yet been performed; and second, to study the above-mentioned dynamic disorder of the water molecules at low temperatures.

Experimental

Single crystals of $Ba(IO_3)_2.H_2O$ were grown by slow interdiffusion of 0.1 M solutions of $BaCl_2$ and HIO_3

Table 2. *Atomic coordinates and anisotropic displacement parameters* U_{ij}(Å² × 10⁻²) *for* $Ba(IO_3)_2.H_2O$ *and* $Pb(ClO_3)_2.H_2O$ *with e.s.d.'s in parentheses*

The isotropically refined atom is marked with an asterisk.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ba(IO₃)₂.H₂O, neutron data, 295 K									
Ba	0.0	0.3912 (2)	0.25	1.52 (8)	1.39 (8)	1.52 (7)	0.0	0.18 (6)	0.0
I	0.2592 (1)	0.2837 (2)	0.5618 (1)	1.35 (6)	1.33 (6)	1.07 (5)	0.09 (4)	0.03 (4)	0.09 (4)
O(1)	0.0664 (1)	0.3402 (2)	0.5636 (1)	1.65 (6)	2.17 (6)	2.41 (6)	0.57 (4)	0.05 (4)	−0.07 (4)
O(2)	0.2577 (1)	0.0930 (2)	0.6608 (1)	2.11 (6)	2.31 (7)	2.61 (6)	0.50 (5)	0.45 (5)	1.07 (5)
O(3)	0.2624 (1)	0.1997 (2)	0.3950 (1)	2.35 (6)	3.14 (6)	1.43 (6)	0.45 (5)	0.12 (5)	−0.43 (5)
O(4)	0.0	0.0515 (3)	0.25	2.30 (12)	1.96 (10)	10.39 (23)	0.0	0.94 (13)	0.0
H	0.0783 (3)	−0.0100 (4)	0.2179 (3)	3.70 (15)	3.93 (14)	5.54 (15)	0.70 (13)	0.13 (12)	0.44 (12)
Ba(IO₃)₂.H₂O, X-ray data, 25 K									
Ba	0.0	0.39033 (2)	0.25	0.690 (9)	0.139 (8)	0.410 (8)	0.0	0.369 (5)	0.0
I	0.25915 (2)	0.28551 (2)	0.56240 (1)	0.864 (9)	0.193 (7)	0.263 (8)	0.126 (3)	0.355 (5)	0.054 (3)
O(1)	0.0650 (2)	0.3413 (2)	0.5634 (2)	0.96 (6)	0.67 (6)	0.78 (6)	0.23 (5)	0.31 (5)	0.07 (5)
O(2)	0.2573 (2)	0.0927 (3)	0.6626 (2)	1.45 (8)	0.58 (6)	1.24 (8)	0.46 (5)	0.85 (6)	0.64 (5)
O(3)	0.2617 (2)	0.1997 (3)	0.3944 (2)	1.30 (7)	1.00 (7)	0.59 (6)	0.17 (6)	0.33 (5)	−0.28 (5)
O(4)	0.0019 (14)	0.0506 (5)	0.2688 (6)	1.13 (13)	0.64 (11)	1.72 (40)	0.12 (14)	−0.09 (33)	−0.22 (21)
H	0.081 (4)	−0.002 (6)	0.205 (4)	0.86 (8)*					
Pb(ClO₃)₂.H₂O, neutron data, 295 K, crystal (I)									
Pb	0.0	0.3707 (1)	0.25	1.87 (6)	2.22 (6)	2.53 (6)	0.0	0.38 (5)	0.0
Cl	0.2430 (1)	0.2691 (1)	0.5525 (1)	1.35 (5)	1.83 (4)	1.59 (4)	0.02 (3)	0.20 (3)	0.08 (3)
O(1)	0.0842 (2)	0.3341 (2)	0.5521 (2)	1.80 (7)	3.13 (8)	2.99 (8)	0.68 (6)	0.39 (5)	0.07 (6)
O(2)	0.2493 (2)	0.1048 (2)	0.6342 (2)	2.75 (8)	2.45 (7)	2.53 (8)	0.38 (6)	0.63 (6)	0.76 (5)
O(3)	0.2652 (2)	0.2273 (2)	0.3951 (1)	2.47 (8)	3.75 (9)	1.57 (7)	0.48 (6)	0.45 (5)	0.02 (6)
O(4)	0.0	0.0597 (3)	0.25	2.32 (14)	2.28 (12)	8.20 (19)	0.0	2.06 (13)	0.0
H	0.0770 (3)	−0.0068 (4)	0.2107 (4)	3.83 (18)	4.01 (16)	7.15 (19)	0.83 (13)	1.38 (16)	−0.19 (14)
Pb(ClO₃)₂.H₂O, neutron data, 295 K, crystal (II)									
Pb	0.0	0.3704 (2)	0.25	1.85 (7)	2.06 (7)	2.51 (8)	0.0	0.41 (6)	0.0
Cl	0.2432 (1)	0.2691 (1)	0.5527 (1)	1.33 (5)	1.67 (5)	1.49 (5)	0.04 (3)	0.30 (3)	0.08 (4)
O(1)	0.0839 (2)	0.3342 (2)	0.5521 (2)	1.68 (9)	3.01 (10)	2.98 (10)	0.73 (7)	0.43 (7)	0.18 (7)
O(2)	0.2488 (2)	0.1047 (2)	0.6344 (2)	2.68 (9)	2.33 (9)	2.55 (10)	0.50 (7)	0.79 (7)	0.73 (7)
O(3)	0.2653 (2)	0.2271 (2)	0.3951 (2)	2.37 (10)	3.57 (10)	1.59 (9)	0.38 (7)	0.56 (6)	−0.04 (7)
O(4)	0.0	0.0596 (4)	0.25	2.31 (18)	2.02 (15)	8.06 (24)	0.0	2.00 (16)	0.0
H	0.0769 (4)	−0.0064 (5)	0.2106 (4)	3.63 (21)	4.02 (20)	6.80 (24)	0.82 (17)	1.72 (18)	−0.38 (17)
Pb(ClO₃)₂.H₂O, neutron data, 25 K									
Pb	0.0	0.37176 (9)	0.25	0.50 (3)	0.53 (3)	0.30 (4)	0.0	0.06 (3)	0.0
Cl	0.24396 (6)	0.27149 (6)	0.55319 (6)	0.52 (3)	0.58 (3)	0.37 (3)	−0.02 (2)	0.04 (2)	0.01 (2)
O(1)	0.08309 (9)	0.33637 (11)	0.55305 (10)	0.70 (4)	0.98 (4)	0.75 (5)	0.14 (3)	0.04 (3)	0.08 (3)
O(2)	0.24496 (9)	0.10460 (11)	0.63549 (9)	0.87 (4)	0.77 (4)	0.69 (4)	0.04 (3)	0.13 (3)	0.20 (3)
O(3)	0.26575 (9)	0.22869 (11)	0.39444 (10)	0.91 (4)	1.04 (4)	0.41 (4)	0.11 (3)	0.12 (3)	0.05 (3)
O(4)	0.0	0.05897 (16)	0.25	0.86 (6)	0.77 (5)	2.10 (7)	0.0	0.57 (6)	0.0
H	0.0785 (2)	−0.0105 (2)	0.2097 (2)	2.39 (9)	2.13 (8)	3.63 (11)	0.57 (7)	0.91 (8)	−0.19 (7)

through a sodium silicate gel in U-shaped tubes at room temperature. Owing to the very limited solubility of Ba(IO₃)₂.H₂O, the size of the crystals was rather small and thus required a high-flux neutron source. Neutron diffraction data at room temperature and X-ray data at 25 K were collected.

In contrast, the very good solubility of Pb(ClO₃)₂.H₂O made it possible to grow quite large crystals by evaporation of an aqueous solution at room temperature. These were generally slightly opaque and not of the excellent optical quality shown by those of Ba(IO₃)₂.H₂O, but during the refinements this turned out to be an advantage (see the discussion below). Two neutron diffraction data sets were collected at room temperature from two different crystals, and one neutron data set at 25 K, with ω–2θ scans. Experimental details for all data collections are given in Table 1.

The atomic positions from the room-temperature X-ray refinements (Lutz, Alici & Buchmeier, 1986) were taken as starting values in all cases. The refinements were performed either with a modified

SHELX program (Sheldrick, 1976) or with the *DUPALS* set of programs (Lundgren, 1982). Neutron scattering lengths for all atoms were taken from Sears (1986) and X-ray scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV). All refinements were based on F^2 and considered converged when Δ/σ was less than 0.001. Weights were assigned according to $w = [\sigma(F^2) + (kF^2)^2]^{-1}$. Details of the data processing and refinement procedures are given in Table 1. A refinement of the 25 K Ba(IO₃)₂.H₂O X-ray data with a single position for the water O atom, which was performed for comparison, gave $wR = 0.0456$, indicating an improvement of the split-position model according to Hamilton's (1964) R-factor ratio test. The same conclusion is drawn from the final Fourier and difference Fourier maps. The H-atom coordinates could only be refined assuming a single position with the isotropic temperature factor fixed to $B_{iso} = 1.0$ Å². Distances and angles involving the H atoms are included in Table 3 for comparison, but they do not form a basis for the following discussion.

Table 3. Selected bond lengths (Å) and angles (°) with e.s.d.'s in parentheses

In the column entitled $Pb(ClO_3)_2.H_2O$, 295 K, the average values from both data sets are given

	Ba(IO₃)₂.H₂O		Pb(ClO₃)₂.H₂O		Symmetry operations
	295 K	25 K	295 K	25 K	
Metal coordination					
M—O(1)	3.170 (1)	3.149 (2)	2.831 (2)	2.831 (1)	o—o, o—iii
M—O(1)	2.908 (2)	2.890 (2)	3.032 (2)	2.993 (1)	o—i, o—ii
M—O(2)	2.835 (1)	2.824 (2)	3.007 (2)	2.968 (1)	o—iv, o—v
M—O(3)	3.129 (1)	3.104 (2)	2.848 (2)	2.829 (1)	o—o, o—iii
M—O(3)	2.728 (1)	2.719 (2)	2.628 (2)	2.620 (1)	o—vi, o—vii
M—O(4)	2.713 (3)	2.703 (4)	2.408 (3)	2.408 (1)	o—o
Halate ions					
X—O(1)	1.803 (1)	1.807 (2)	1.489 (2)	1.494 (1)	o—o
X—O(2)	1.812 (2)	1.823 (2)	1.475 (2)	1.488 (1)	o—o
X—O(3)	1.785 (2)	1.793 (2)	1.497 (2)	1.511 (1)	o—o
O(1)—X—O(2)	100.27 (8)	100.01 (9)	107.5 (1)	107.20 (6)	o—o—o
O(1)—X—O(3)	98.76 (6)	98.31 (9)	104.1 (1)	104.21 (6)	o—o—o
O(2)—X—O(3)	100.73 (10)	100.57 (9)	107.2 (1)	107.05 (6)	o—o—o
X···X	3.779 (2)	3.755 (1)	3.613 (2)	3.604 (1)	o···x
Water molecules and hydrogen bonds					
O(4)—H	0.928 (3)	0.90 (4), 1.05 (4)	0.938 (4)	0.961 (2)	o—o, o—iii
O(4)—H*	–	1.05 (4), 0.90 (4)	–	–	iii—o, iii—iii
H—O(4)—H	116.1 (4)	125 (5)	113.6 (4)	112.7 (3)	o—o—iii
H···H	1.575 (6)	1.74 (8)	1.569 (7)	1.600 (4)	o—iii
H···O(2)	1.861 (3)	1.81 (4)	1.866 (4)	1.834 (2)	o—viii, iii—ix
O(4)—H···O(2)	168.1 (3)	157 (3), 175 (4)	170.5 (4)	169.2 (2)	o—o—viii, o—iii—ix
O(4)—H···O(2)*	–	175 (4), 157 (3)	–	–	iii—o—viii, iii—iii—ix
M—O(4)—H	122.0 (2)	111 (2), 119 (3)	123.2 (2)	123.6 (1)	o—o—o, o—o—iii
M—O(4)—H*	–	119 (3), 111 (2)	–	–	o—iii—o, o—iii—iii
O(4)···O(4)	–	0.371 (11)	–	–	o—iii

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

* Owing to the splitting of the O-atom position in Ba(IO₃)₂.H₂O at 25 K, these distances occur here twice compared to the remaining determinations.

Atomic coordinates and thermal parameters are listed in Table 2,* selected bond lengths and angles are given in Table 3.

Discussion

A general description of the structure type has already been given (Lutz, Alici & Buchmeier, 1986). Therefore, the following discussion will be restricted to only those aspects which arise from a comparison of the data obtained from two independent room-temperature neutron diffraction studies on two different crystals of $Pb(ClO_3)_2.H_2O$, and from the X-ray and neutron studies at two different temperatures of the title compounds.

Inter-experimental agreement

From a comparison of the two room-temperature parameter sets for $Pb(ClO_3)_2.H_2O$, an excellent inter-experimental agreement is found. The χ^2 test (Hamilton, 1964) indicates that the hypothesis that the two parameter sets are identical can be accepted at the 99.5% level, because the tabulated value of $\chi^2_{(56, 0.995)} = 31.96 > 25.15$ as calculated for the actual example.

A more quantitative evaluation of the agreement can be made by inspection of a half-normal probability δp plot according to Abrahams & Keve (1971), where the 56 positional and anisotropic thermal parameters are compared individually in terms of their combined standard deviations (see Fig. 1). Since the structure is centrosymmetric, the relative signs of the differences are not relevant. The array is close to linear, the least-squares line has a slope of 0.75, indicating that the individual standard deviations have been underestimated by ca 25%, and an ordinate intercept of -0.06. It can therefore be concluded that random errors are predominant and systematic errors are small. The thermal parameters especially seem to be quite reliable, which cannot always be claimed for neutron data, since extinction is frequently a serious problem for the relatively large crystals which must be used if no high-flux facilities are available. In the present case, however, the small values of the refined extinction parameters, isotropic as well as anisotropic models (see Table 1), already indicated that extinction was not too large. Additionally, this view is supported by the fact that the two crystals had quite different sizes.

Bonding of the water molecule

The coordination of the single water molecule in this structure type – or more precisely, of the average water molecule at room temperature – is ideally

trigonal planar with the metal atom and the water O atom being located on a twofold axis. Such a trigonal coordination mode has not yet been observed in any other Sr^{2+}, Ba^{2+} or Pb^{2+} salt hydrates. The hydrogen bonds are relatively weak as shown from both the long H$\cdots$O distances (see Table 3) and the high OH (OD) stretching frequencies in isotopically dilute samples (Lutz, Christian & Eckers, 1985; Henning, 1988). Therefore it is likely that hydrogen bonds are in this case not determinative for the overall structure, a view which is supported by the fact that α-Ba(IO$_3$)$_2$ (Petříček, Malý, Kratchovíl, Podlahová & Loub, 1980) and additionally one polymorphic form of both Ba(BrO$_3$)$_2$ and Sr(IO$_3$)$_2$ (Lutz, Alici, Kellersohn & Kuske, 1990) crystallize in a structure which is very closely related to the Ba(ClO$_3$)$_2$.H$_2$O type but with the water position not occupied. Therefore it seems that in the compounds of this structure type the water molecule has to confine itself in a given structure site which does not in all respects satisfy its bonding preferences, which causes the observed 'structural instabilities' at room temperature. However, such a specific situation does not seem to be a necessary prerequisite for these instabilities, since, for example, in CoSO$_4$.7D$_2$O (Kellersohn, Delaplane & Olovsson, 1991) one of the water molecules in an otherwise regular [Co(D$_2$O)$_6$]$^{2+}$ octahedron exhibits a very similar behaviour. More likely the polarizing properties of the cation seem to be of importance, as will be seen below.

Room-temperature data

The vibrational ellipsoids of the water molecule (all derived from room-temperature neutron data) in Ba(ClO$_3$)$_2$.H$_2$O, Sr(BrO$_3$)$_2$.H$_2$O, Sr(IO$_3$)$_2$.H$_2$O, Pb(ClO$_3$)$_2$.H$_2$O and Ba(IO$_3$)$_2$.H$_2$O are shown in Figs. 2(a)–2(d) and 2(f) on the same scale. The similarity between all compounds is striking, and is also shown by the numerical values of the displacement parameters [for the data not given here see Sikka, Momin, Rajagopal & Chidambaram (1968), Kellersohn, Lutz, Gonschorek & Weitzel (1990) and Lutz, Kellersohn & Vogt (1990)]. In all cases the root-mean-square displacement of the water O normal to the HOH plane is larger than the respective values for the H atoms connected to it, which indicates that the 'structural instability' mentioned above involves mainly the O atom. This vibrational behaviour is untypical for solid hydrates; see the survey of thermal parameters for water molecules given by Eriksson & Hermansson (1983).

A consequence of this is that the apparent HOH bond angles derived from the room-temperature data are systematically too large, cf. Eriksson, Berglund, Tegenfeldt & Lindgren (1979). Any 'riding' model,

which attempts to correct bond lengths and angles, fails to account for this peculiarity. The uncorrected HOH angle for Ba(IO$_3$)$_2$.H$_2$O at 295 K would represent the largest one reported so far for solid hydrates. Assuming a non-resolvable split position of the O atom with a mean separation of 0.25 Å for the nuclei yields a rough estimate of $-2.5°$ for the correction for vibrational motion. Nevertheless, the correspondingly corrected HOH angles are at the upper limit of the range reported for solid hydrates (Chiari & Ferraris, 1982), and the HOH angle determined for Pb(ClO$_3$)$_2$.H$_2$O at 25 K still has a large value of 112.7 (3)°. Therefore, it seems that the large angles found at room temperature are not entirely artifacts. Whether this can be related to electronic effects, as suggested by Lutz, Kellersohn & Vogt (1990), cannot be decided unambiguously, since there are too many heavy atoms in all the compounds to perform a meaningful electron density study.

Low-temperature data

The distortion of the halate ions from C_{3v} symmetry, as derived from the differences of the X—O bond lengths and O—X—O angles (see Table 3), is maintained at low temperatures. The X—O bond lengths seem to increase uniformly compared with the room-temperature data, which are in full agreement with the 'riding' model, and therefore this increase is only apparent.

The main result from the low-temperature structure refinements is the observation that the water O atom in Pb(ClO$_3$)$_2$.H$_2$O remains in a trigonal coordi-
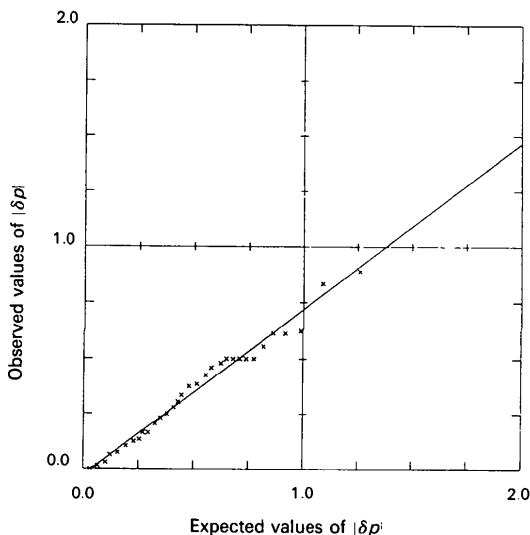

Fig. 1. Half-normal probability plot comparing the positional and anisotropic thermal parameters from the two independent structure determinations of Pb(ClO$_3$)$_2$.H$_2$O at room temperature.
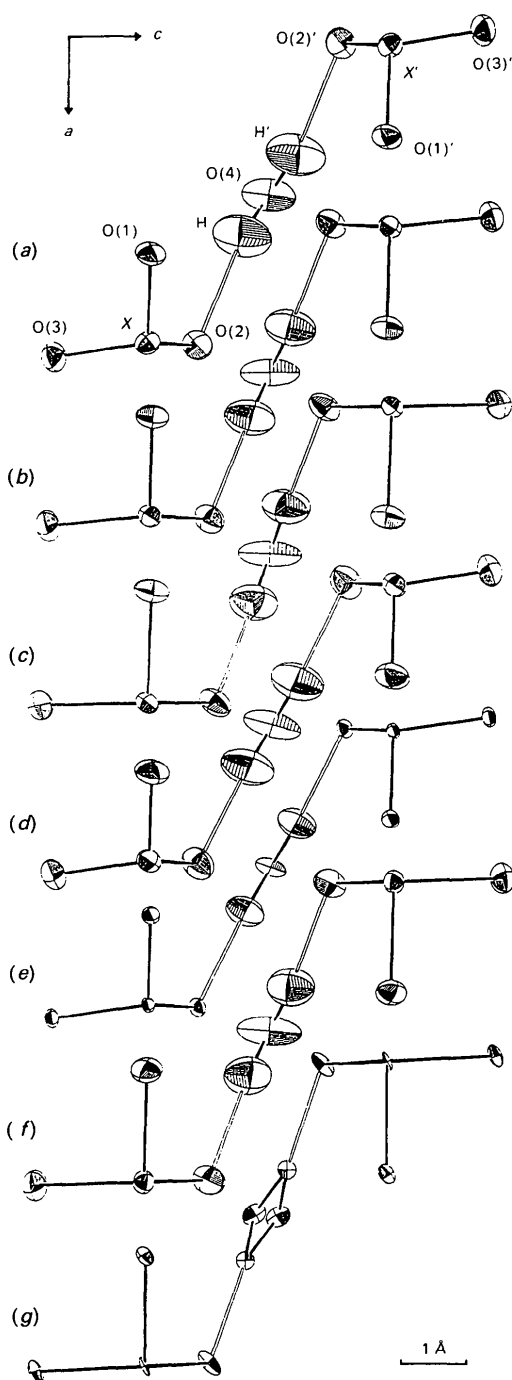
Fig. 2. The water molecule and the hydrogen-bond-accepting halate ions of (a) $Ba(ClO_3)_2.H_2O$, (b) $Sr(BrO_3)_2.H_2O$, (c) $Sr(IO_3)_2.H_2O$, (d) $Pb(ClO_3)_2.H_2O$, average of the two parameter sets, (e) $Pb(ClO_3)_2.H_2O$, 25 K, (f) $Ba(IO_3)_2.H_2O$, (g) $Ba(IO_3)_2.H_2O$, 25 K, X-ray data. The view is along the [010] direction. The scale given in the lower right corner applies for all parts of the figure, as does the labelling of (a) (X = Cl, Br, I). Primes indicate atoms related by the twofold axis. Hydrogen bonds are drawn as open lines. The vibrational ellipsoids (Johnson, 1976) include 50% probability except in (g) where the H atoms are given arbitrary radii. Room-temperature neutron data unless otherwise stated.

nation with a diminished anisotropy of the thermal ellipsoid compared to room temperature (Figs. 2d and e), whereas in $Ba(IO_3)_2.H_2O$ it freezes on a split position on both sides of the twofold axis as an approach to the preferred tetrahedral coordination (Figs. 2f and g). Only a single H-atom position could be refined from the X-ray data, but it is likely that the statistical disorder at 25 K involves, at least to some degree, the H atoms as well. However, this is beyond the limit of the information that X-ray data can provide.

These results are somewhat unexpected, since the vibrational spectra show a very similar temperature dependence, and it was therefore thought that the ordering process would be the same for all compounds on an atomic scale. However, it could not be decided whether the freezing leads to a single- or double-minimum potential. The diffraction results show that both possibilities can be realized within the same structure type. The reason for this difference might be the different polarizing power of the metal ions, which is smaller for Ba^{2+} than for Pb^{2+}. This can already be inferred from the different charge-to-radius ratio and from the shorter Pb—O distances compared to Ba—O, see Table 3. A more quantitative impression of this difference is given by IR and Raman spectra of samples which, in addition to ca 7% D_2O, contain a small amount of metal guest ions. For Pb^{2+} in $Ba(ClO_3)_2.H_2O$, an additional frequency downshift of 63 cm^{-1} is observed, whereas the opposite case leads to an upshift of 79 cm^{-1}. These values indicate the different metal–oxygen interaction strengths separately, since the effects of different O···O distances are largely eliminated through the double matrix-isolation technique employed (Lutz & Henning, 1987; Lutz, 1988).

The trigonal coordination of water molecules occurs generally in the presence of highly charged small cations, but it has not been found for e.g. alkali metals or hydrogen bonds on the O-atom lone-pair side. $Ba(ClO_3)_2.H_2O$-type compounds represent a borderline case in this respect, which has already been recognized. Now it can be suggested that this borderline lies between Pb and Ba. The behaviour of the water molecules in the Sr compounds cannot be predicted from the available data. Further low-temperature studies are therefore desirable.

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Berechnung der Anzahl möglicher Strukturtypen für Verbindungen mit dichtest gepackter Anionenteilstruktur. I. Das Rechenverfahren

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Abstract

For compounds $A_aB_bC_c...X_xY_yZ_z...$, in which the atoms X, Y, Z... form a close-packed arrangement and the remaining atoms occupy voids of this packing, a general procedure to calculate the number of possible structure types depending on space-group symmetry is given. The calculation follows White's theorem as stated by McLarnan [*Z. Kristallogr.* (1981), 155, 227–245]. Crystallographic group–subgroup relationships and specifically the numbers of conjugate subgroups have to be considered; special problems concerning conjugate subgroups are outlined. As an example, a calculation is presented for hexagonal close-packing of X atoms and other atoms occupying octahedral voids for possible structure types having a unit cell that is enlarged by a factor of three relative to the close-packing unit cell (H cell).

Einleitung

Bei der systematischen Erfassung und Ordnung von Kristallstrukturen ist es nützlich, auch in der Natur noch nicht aufgefundene Strukturtypen zu betrachten. Deren Kenntnis kann nicht nur bei der Strukturbestimmung neuer Verbindungen hilfreich sein, sondern durch Vergleich mit bekannten Strukturen können Gesetzmäßigkeiten für das Auftreten bestimmter Strukturmerkmale aufgedeckt werden. Die Herleitung möglicher, hypothetischer wie auch bekannter Strukturtypen kann durch ein systematisches Durchprobieren aller Varianten unter Einhaltung bestimmter Bedingungen erfolgen. Dies ist für eine Reihe von Verbindungstypen bereits durchgeführt worden. Für Verbindungen M_mX_n, bei denen die X Atome für sich eine dichteste Kugelpackung bilden, sind unter anderen folgende Arbeiten zu nennen: Beck (1967); Deblieck,