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Comparative Study of the Crystal Structures of Isotypic $MX_2.H_2O$, M = Sr, Ba, and X = Cl, Br, I. Bifurcated H Bonds in Solid Hydrates

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Abstract

$SrCl_2.H_2O$: $M_r = 176{\cdot}54$, $a = 10{\cdot}881\,(1)$, $b = 4{\cdot}162\,(1)$, $c = 8{\cdot}864\,(1)$ Å, $V = 401{\cdot}4\,(1)$ Å^3, $D_x = 2{\cdot}921$ Mg m^{-3}, $\mu = 14{\cdot}16$ mm^{-1}, $F(000) = 328$, $R = 0{\cdot}025$ for 1103 unique reflections; $SrBr_2.H_2O$: $M_r = 265{\cdot}46$, $a = 11{\cdot}464\,(1)$, $b = 4{\cdot}295\,(1)$, $c = 9{\cdot}229\,(1)$ Å, $V = 454{\cdot}4\,(1)$ Å^3, $D_x = 3{\cdot}880$ Mg m^{-3}, $\mu = 28{\cdot}75$ mm^{-1}, $F(000) = 472$, $R = 0{\cdot}060$ for 763 reflections; $SrI_2.H_2O$: $M_r = 359{\cdot}44$, $a = 12{\cdot}474\,(2)$, $b = 4{\cdot}495\,(1)$, $c = 9{\cdot}741\,(2)$ Å, $V = 546{\cdot}2\,(1)$ Å^3, $D_x = 4{\cdot}370$ Mg m^{-3}, $\mu = 20{\cdot}62$ mm^{-1}, $F(000) = 616$, $R = 0{\cdot}043$ for 966 reflections; $BaCl_2.H_2O$: $M_r = 226{\cdot}26$, $a = 11{\cdot}094\,(1)$, $b = 4{\cdot}500\,(1)$, $c = 9{\cdot}054\,(1)$ Å, $V = 452{\cdot}0\,(1)$ Å^3, $D_x = 3{\cdot}324$ Mg m^{-3}, $\mu = 9{\cdot}79$ mm^{-1}, $F(000) = 400$, $R = 0{\cdot}021$ for 1231 reflections; $BaBr_2.H_2O$: $M_r = 315{\cdot}18$, $a = 11{\cdot}643\,(2)$, $b = 4{\cdot}604\,(1)$, $c = 9{\cdot}438\,(2)$ Å, $V = 505{\cdot}9\,(1)$ Å^3, $D_x = 4{\cdot}137$ Mg m^{-3}, $\mu = 23{\cdot}34$ mm^{-1}, $F(000) = 544$, $R = 0{\cdot}040$ for 1098 reflections; $BaI_2.H_2O$: $M_r = 409{\cdot}16$, $a = 12{\cdot}494\,(1)$, $b = 4{\cdot}772\,(1)$, $c = 10{\cdot}014\,(1)$ Å, $V = 597{\cdot}1\,(1)$ Å^3, $D_x = 4{\cdot}551$ Mg m^{-3}, $\mu = 16{\cdot}75$ mm^{-1}, $F(000) = 688$, $R = 0{\cdot}023$ for 935 reflections; all orthorhombic, $Pnma$ (D_{2h}^{16}), $Z = 4$, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å and $T = 293$ K. The structures consist of distorted face-sharing $MX_7(H_2O)_2$ tricapped trigonal prisms forming columns and channels along [010]. The distortion of the water molecules, which form weak,

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Table 1. *Summary of crystal data, intensity measurement and structure refinement*

	$SrCl_2.H_2O$	$SrBr_2.H_2O$	$SrI_2.H_2O$	$BaCl_2.H_2O$	$BaBr_2.H_2O$	$BaI_2.H_2O$
Crystal-growth temperature (K)	400	370*	400	340	380	390
Unit-cell determination						
radiation	Cu $K\alpha_1$	Cr $K\alpha_1$	Cr $K\alpha_1$	Cr $K\alpha_1$	Cr $K\alpha_1$	Cr $K\alpha_1$
number of reflections	70	49	19	38	22	27
θ range (°)	6-41	9-44	17-45	9-50	9-43	8-50
Number of reflections measured	1358	1103	1824	1993	1684	1998
Number of unique reflections	1103	763	966	1231	1098	935
Number of unobserved reflections	255	340	858	762	586	1063
$2\theta_{max}$ (°)	80	70	80	90	80	80
Maximum $(\sin\theta/\lambda)$ (Å^{-1})	0·9042	0·8060	0·9034	0·9937	0·9026	0·9039
Range of h	0-19	0-18	0-22	0-21	0-20	0-21
Range of k	0-7	0-6	0-8	0-8	0-8	0-8
Range of l	0-15	0-14	0-17	0-17	0-16	0-17
Standard reflections	702	404	702	721	702	503
	302	312	302	610	312	214
	216	—	614	614	116	722
Intensity variation	(1-0·95)	none	1-0·91	1-0·95	1-0·98	1-0·96
Transmission factors	1-0·501	1-0·148	1-0·464	1-0·680	1-0·268	1-0·657
Number of parameters	32	25	25	32	26	26
R	0·025	0·060	0·043	0·021	0·040	0·023
wR	0·026	0·064	0·045	0·023	0·043	0·026
S	0·74	3·50	3·16	0·96	2·42	2·13
Extinction coefficients ($\times 10^{-7}$)	12·1 (2)	—	—	5·4 (1)	1·80 (9)	1·89 (3)
$(\Delta/\sigma)_{max}$	<0·01	<0·01	<0·01	<0·01	<0·01	<0·01
$(\Delta\rho)_{max}$ (e Å^{-3})	1·3 (2)	2·6 (5)	6·4 (4)	2·1 (2)	3·1 (4)	1·1 (3)

* From aqueous solution.

bifurcated H bonds to halide ions, decreases with increasing ratio of the ionic radii r_X/r_M. The positive temperature shift of the stretching mode of one OH bond of the H_2O molecule in $BaCl_2.H_2O$, observed despite the bifurcated H bond, is caused by the fact that both the distances to the two chloride ions acting as H-bond acceptor groups are equal and the donor (O), the two acceptor groups and the H atom are nearly in one plane (a 'symmetric bifurcated' H bond). The OH modes of all other H atoms in the hydrates under discussion reveal negative temperature shifts as predicted for bifurcated H bonds by Falk, Huang & Knop [*Can. J. Chem.* (1974), **52**, 2380-2388].

Introduction

As part of spectroscopic studies on the bonding structure of water molecules in solid hydrates, we analysed the infrared and Raman spectra of the alkaline-earth halide monohydrates $MX_2.H_2O$ with M = Sr, Ba, and X = Cl, Br and I (Lutz & Christian, 1982). From these experiments it was revealed that the two H-atom positions in the structures of these isostructural compounds ($BaCl_2.H_2O$ type) (Lutz, Klüppel & Kho, 1971; Lutz, Klüppel, Marner & Kesterke, 1973; Engelen, Freiburg & Lutz, 1983) are energetically equivalent in the case of the iodides, *i.e.* the site symmetry of the water molecules is $mm2$ (C_{2v}), but different for the bromides and chlorides. This was shown by observing only one OH stretching mode of the HDO molecules in isotopically dilute samples of the iodides and two OH stretching modes in those of the chlorides and bromides.

Because crystal structure data were only available for $BaCl_2.H_2O$ and $BaBr_2.H_2O$ from electron diffraction studies of thin layers (Vajnstejn & Pinsker, 1949, 1950) and for $SrBr_2.H_2O$ from single-crystal X-ray measurements (Dyke & Sass, 1964), and these data were not accurate enough to explain the reason for this trend, we determined or redetermined the crystal structures of all the halide monohydrates under discussion in order to analyse the lengths of the H bonds, especially the trend on going from the chlorides to the iodides. Initial results for $SrCl_2.H_2O$ and $SrBr_2.H_2O$ are given in Engelen, Freiburg & Lutz (1983).

Furthermore, the spectroscopic studies (Lutz & Christian, 1982) revealed that the H bonds present are bifurcated with the exception of one H atom in $BaCl_2.H_2O$, for which the positive temperature shift of the corresponding OH stretching modes predicted a linear H bond (Falk, Huang & Knop, 1974). This finding was not consistent with the crystal structure of this compound. We therefore also determined the H-atom positions, as far as possible from X-ray data.

Experimental

Single crystals of the monohydrates under investigation were prepared by heating aqueous suspensions of the higher hydrates in glass tubes under a nitrogen stream in order to remove the water vapour at temperatures given in Table 1. The dry residues were placed in an argon glove box and mixed with paraffin oil to separate the crystals from powdery material. Polycrystalline samples were obtained by rehydration of the anhydrous salts with stoichiometric amounts of H_2O (Lutz, Becker, Mertins & Engelen, 1979).

The plate-like crystals (0·3 × 0·3 × 0·1 mm) were mounted in sealed glass capillaries on an Enraf-Nonius CAD-4 diffractometer. The intensities of the reflections were measured by ω-2θ scans with graphite-monochromatized Mo $K\alpha$ radiation and corrected for Lorentz and polarization effects. An empirical correction for absorption (North, Phillips & Mathews, 1968) was made by ψ scans, and for intensity decrease by measuring three standard reflections. Reflections with $I > 2\sigma_I$ (σ_I from counting statistics) were considered as observed.

The M and X positions were determined from Patterson syntheses, the O positions from subsequent electron density summations. Scattering factors for M^0, X^0, and O^0 were from *International Tables for X-ray Crystallography* (1974). In the case of the chlorides, we could locate the H atoms by difference Fourier syntheses. Full-matrix least-squares refinements of positional, anisotropic (M, X, O) and isotropic (H) thermal parameters, extinction coefficients, and scale factors are based on the F magnitudes of the observed reflections (Enraf-Nonius, 1982); weighting scheme $w = 1/\sigma_I$.

The experimental data and structure refinement are summarized in Table 1. The final atomic coordinates and thermal parameters are given in Table 2.* The cell parameters were determined by least-squares methods from Guinier powder data (Huber FR 600 system, Cr $K\alpha_1$ radiation, α-quartz as an internal standard, $a = 4{\cdot}9136$, $c = 5{\cdot}4054$ Å, number and θ range of reflections used see Table 1).

Discussion

The crystal structures of some $BaCl_2.H_2O$-type compounds are shown in Figs. 1–3. M, $X(1)$, $X(2)$, O, H(1) and H(2) all occupy the special position 4c of the space group *Pnma*. The metal ions are coordinated by seven halide ions and two H_2O molecules in the form of distorted tricapped trigonal prisms (see Fig. 1). The M–X and M–O distances (see Table 3) are similar to those of other halide hydrates. The $MX_7(H_2O)_2$ polyhedra share faces with common triangular basal planes forming $[MX_5(H_2O)]_n$ columns parallel to [010], which are edge-connected with common X^- ions in such a manner that channel-like cavities are formed along [010] (see Fig. 2). The H atoms, which form weak, bifurcated H bonds to adjacent halide ions (see Fig. 3), are in these channels as concluded from NMR and infrared data (McGrath & Silvidi, 1960; Lutz & Christian, 1982). The coordination of the water molecules is type B after Chidambaram, Sequeira & Sikka (1964). Additional structure details are given in Vajnstejn & Pinsker (1949, 1950), Dyke & Sass (1964) and Engelen, Freiburg & Lutz (1983).

Table 2. *Fractional coordinates and equivalent isotropic temperature factors* ($Å^2 \times 10^2$) *with e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{3}\textstyle\sum_i \sum_j U_{ij}$$

	x	y	z	U_{eq}
$SrCl_2.H_2O$				
Sr	0·18774 (3)	0·25	0·10312 (3)	1·798 (5)
Cl(1)	0·10005 (6)	0·75	−0·11547 (8)	1·93 (1)
Cl(2)	0·12340 (6)	0·75	0·33206 (8)	1·83 (1)
O	0·3382 (2)	0·75	0·1016 (3)	2·06 (4)
H(1)	0·385 (5)	0·75	0·159 (6)	5 (1)
H(2)	0·369 (5)	0·75	0·027 (7)	6 (3)
$SrBr_2.H_2O$				
Sr	0·1897 (1)	0·25	0·1134 (2)	1·85 (3)
Br(1)	0·1015 (1)	0·75	−0·1138 (2)	1·85 (3)
Br(2)	0·1156 (1)	0·75	0·3463 (2)	1·80 (3)
O	0·326 (1)	0·75	0·114 (1)	2·1 (2)
$SrI_2.H_2O$				
Sr	0·1967 (1)	0·25	0·1208 (2)	2·43 (3)
I(1)	0·10358 (7)	0·75	−0·11399 (8)	1·93 (2)
I(2)	0·10784 (7)	0·75	0·35664 (8)	2·08 (2)
O	0·3129 (6)	0·75	0·125 (1)	1·7 (2)
$BaCl_2.H_2O$				
Ba	0·18996 (2)	0·25	0·10619 (3)	1·738 (3)
Cl(1)	0·10199 (8)	0·75	−0·1197 (1)	2·12 (2)
Cl(2)	0·12343 (8)	0·75	0·3353 (1)	2·12 (2)
O	0·3444 (3)	0·75	0·0997 (4)	2·36 (5)
H(1)	0·386 (6)	0·75	0·148 (7)	5 (3)
H(2)	0·361 (7)	0·75	0·016 (9)	8 (3)
$BaBr_2.H_2O$				
Ba	0·19012 (5)	0·25	0·11634 (6)	1·840 (9)
Br(1)	0·10204 (8)	0·75	−0·1170 (1)	2·09 (2)
Br(2)	0·11620 (8)	0·75	0·3510 (1)	2·16 (2)
O	0·3336 (6)	0·75	0·1130 (9)	2·3 (2)
$BaI_2.H_2O$				
Ba	0·19242 (4)	0·25	0·12215 (6)	1·933 (8)
I(1)	0·10140 (4)	0·75	−0·11759 (6)	2·067 (9)
I(2)	0·10887 (5)	0·75	0·36159 (6)	2·15 (1)
O	0·3210 (5)	0·75	0·1217 (7)	2·5 (1)

The structures of the iodide monohydrates are more symmetric with respect to the H bonds present than those of the bromides and chlorides as predicted in earlier work (Lutz & Christian, 1982; Engelen,

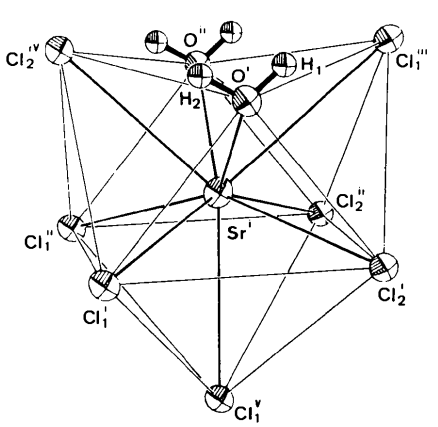

Fig. 1. Coordination of the metal ions in $SrCl_2.H_2O$; for symmetry codes see Table 3.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43265 (67 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester, CH1 2HU, England.

Table 3. *Interatomic distances* (Å) *and angles* (°) *in strontium and barium halide monohydrates*

	$SrCl_2.H_2O$	$SrBr_2.H_2O$	$SrI_2.H_2O$	$BaCl_2.H_2O$	$BaBr_2.H_2O$	$BaI_2.H_2O$
MO_2X_7 polyhedra						
$M^{i}-X(1)^{i/ii}$	2·999 (1)	3·167 (1)	3·411 (1)	3·193 (1)	3·347 (1)	3·571 (1)
$M^{i}-X(1)^{iii}$	3·399 (1)	3·473 (1)	3·589 (1)	3·389 (1)	3·491 (1)	3·664 (1)
$M^{i}-X(1)^{v}$	3·133 (1)	3·339 (1)	3·746 (1)	3·241 (1)	3·402 (1)	3·671 (1)
$M^{i}-X(2)^{i/ii}$	2·990 (1)	3·155 (1)	3·400 (1)	3·148 (1)	3·308 (1)	3·540 (1)
$M^{i}-X(2)^{iv}$	3·162 (1)	3·326 (1)	3·545 (1)	3·209 (1)	3·370 (1)	3·602 (1)
$M^{i}-O^{i/ii}$	2·647 (2)	2·659 (4)	2·675 (2)	2·829 (2)	2·845 (3)	2·877 (3)
$O^{i}-O^{ii}$; $X^{i}-X^{ii}$ (= b)	4·162 (1)	4·295 (1)	4·495 (1)	4·500 (1)	4·604 (1)	4·772 (1)
$X(1)^{i/ii}-X(1)^{v}$	3·642 (1)	3·801 (1)	4·082 (1)	3·857 (2)	3·978 (1)	4·202 (1)
$X(1)^{v}-X(2)^{i/ii}$	3·732 (1)	3·925 (1)	4·194 (1)	3·890 (1)	4·078 (1)	4·309 (1)
$X(1)^{i}-X(2)^{i}$	3·975 (1)	4·249 (1)	4·585 (1)	4·126 (1)	4·420 (1)	4·799 (1)
$X(1)^{iii}-X(2)^{i/ii}$	3·688 (1)	3·907 (1)	4·253 (1)	3·809 (1)	4·019 (1)	4·341 (1)
$X(1)^{i/ii}-X(2)^{iv}$	3·688 (1)	3·907 (1)	4·253 (1)	3·809 (1)	4·019 (1)	4·341 (1)
$M^{i}-M^{vi}$ (= b)	4·162 (1)	4·295 (1)	4·495 (1)	4·500 (1)	4·604 (1)	4·772 (1)
Coordination of the H_2O molecules						
$O^{i}-X(1)^{i}$	3·227 (3)	3·325 (6)	3·500 (5)	3·343 (4)	3·462 (5)	3·643 (5)
$O^{i}-X(2)^{i}$	3·104 (3)	3·233 (6)	3·410 (6)	3·250 (4)	3·384 (5)	3·577 (6)
$O^{i}-X(1)^{iii/vii}$	3·328 (2)	3·409 (5)	3·548 (5)	3·446 (3)	3·515 (4)	3·668 (4)
$O^{i}-X(2)^{iv/viii}$	3·196 (2)	3·338 (5)	3·588 (5)	3·304 (3)	3·429 (4)	3·639 (5)
$O^{i}-X(2)^{ix}$	3·159 (3)	3·335 (6)	3·683 (5)	3·151 (3)	3·307 (5)	3·600 (5)
$X(1)^{iii/vii}-X(2)^{ix}$	3·732 (1)	3·925 (1)	4·194 (1)	3·890 (1)	4·078 (1)	4·309 (1)
φ*	155·1 (1)	146.7 (1)	137.0 (1)	158·3 (1)	150·3 (1)	141·1 (1)
$M^{i}-O^{i}-M^{vi}$	103·6 (1)	107·8 (2)	114·3 (2)	105·4 (1)	108·0 (1)	112·1 (1)

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

* Angle between the planes $O^{i}-X(2)^{iv}-X(2)^{viii}$ and $O^{i}-X(1)^{iii}-X(1)^{vii}$ (see Fig. 4).

Freiburg & Lutz, 1983). This is shown from a decrease of both the angle γ, *i.e.* the angle between the plane through $M^{i}M^{vi}O^{i}$ and the line $O^{i}-X(2)^{ix}$ (see Figs. 3 and 4), and the difference of the two H-bond lengths on going from the chlorides to the iodides (see Table 4). The reason for this result is obviously the difference of the radii of the ions involved. Thus, the difference of the two H-bond lengths Δd (see Table 4 and Fig. 3) and therefore the distortion of the water molecules is maximal for the compound with the smallest difference $r_X - r_M$, *i.e.* $BaCl_2.H_2O$, and minimal for the compound with the largest difference $r_X - r_M$, *i.e.* $SrI_2.H_2O$ (see Fig. 5). For the latter, even the H-bond lengths of H(1) and H(2) are reversed as compared with the other monohydrates.

The reason why in the vibrational spectra of isotopically dilute samples of the iodides only one OH and one OD stretching band of the HDO molecules is observed although the H-bond lengths differ is not yet fully clear. However, the influence of the halide ion $X(2)^{ix}$ on the bonding structure of the water molecules (see Figs. 3 and 4), discussed previously (Lutz & Christian, 1982) as the potential reason for the spectroscopic results, decreases in the order chlorides > bromides > iodides, as shown by the distances $O^{i}-X(2)^{ix}$, which increase more than would be expected from the increasing radii of the halide ions (see Table 3). In the case of the structurally similar $SrI_2.2H_2O$ (Buchmeier & Lutz, 1986), each of the four crystallographically different H atoms

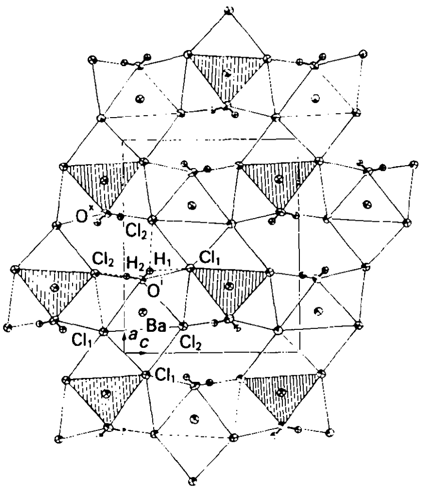

Fig. 2. Arrangement of the $MX_7(H_2O)_2$ polyhedra in $BaCl_2.H_2O$; hatched triangles, mirror planes at y = 0·25 and 1·25; open triangles, mirror planes at y = −0·25 and 0·75; for symmetry codes see Table 3.

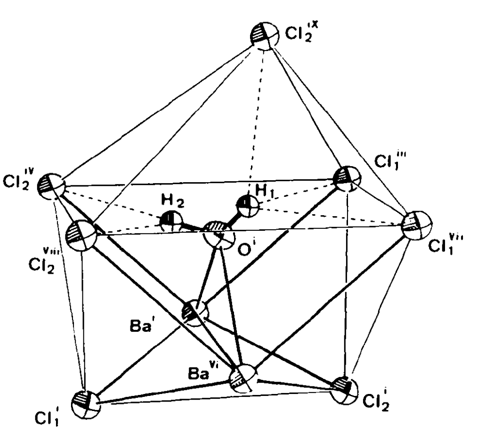

Fig. 3. Coordination of the water molecules in $BaCl_2.H_2O$; dashed lines, H bonds; for symmetry codes see Table 3.

gives rise to a distinct OH (OD) band in the spectra even for nearly equal H-bond lengths, *i.e.* $\Delta d \leq 0{\cdot}04$ Å.

The H-atom positions obtained for the two chlorides reveal that the orientation of the water molecules in the structures is somewhat different (compare Figs. 1 and 3). Whereas the angles α and β, *i.e.* the angles between the O-H(2) and O-H(1) arms of the water molecules and the dashed lines shown in Fig. 4, respectively, of $SrCl_2.H_2O$ are 17 and 30°, the H_2O molecule of $BaCl_2.H_2O$ is rotated in such a manner ($\alpha = 5$, $\beta = 33°$) that the stronger H bond, *i.e.* that of H(2), is strengthened and the weaker bond [H(1)] is weakened. This structural feature also explains the finding that the temperature shift of the OH stretching mode due to H(2) of $BaCl_2.H_2O$ is positive in spite of the bifurcated H bond. The negative temperature shift of the OH and OD stretching modes in the case of bifurcated (or strongly bent) H bonds has been ascribed to the fact that increasing thermal motion tends to straighten and, hence, to strengthen the bent (or bifurcated) H bond (Falk, Huang & Knop, 1974). However, in the case of the H(2) atom of $BaCl_2.H_2O$, thermal motion of the water molecule can only weaken, not strengthen the H bond because H(2) is nearly in the plane O^i-$Cl(2)^{iv}$-$Cl(2)^{viii}$ (see Fig. 3). Such highly 'symmetric bifurcated' H bonds, *i.e.* with both bond lengths equal and a planar arrangement of the two acceptors, the donor and the H atom, must exhibit positive temperature shifts of the OH stretching modes. In this way the concept of Falk, Huang & Knop (1974) has to be modified.

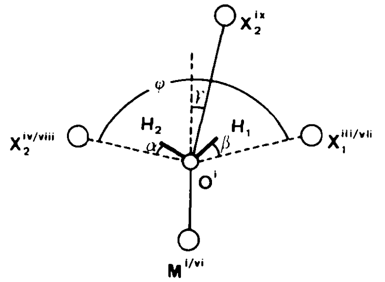

Fig. 4. Environment of the water molecules (see Fig. 3); angle between H(2)-O^i and the plane $X(2)^{iv}$-$X(2)^{viii}$-O^i, α; H(1)-O^i and $X(1)^{iii}$-$X(1)^{vii}$-O^i, β; angle between O^i-$X(2)^{ix}$ and the plane O^i-M^i-M^{vi}, γ; for symmetry codes see Table 3.

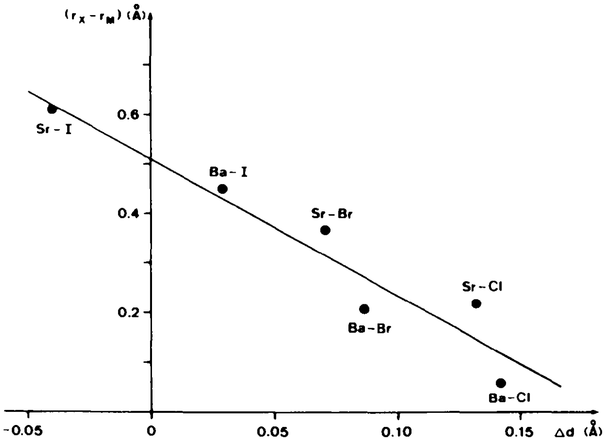

Fig. 5. Differences of the ionic radii $r_X - r_M$ *vs* the differences of the H-bond lengths Δd (see Table 4).

Table 4. *Differences of the* H-*bond lengths, structure distortion, frequency splittings of the* OH *stretching modes, and differences of crystal radii of the alkaline-earth halide monohydrates*

	Δd(Å)	γ(°)	$\Delta\nu_{OH}$ (cm^{-1})	$r_X - r_M$ (Å)
$BaCl_2.H_2O$	0·0142	12·7	88	0·06
$SrCl_2.H_2O$	0·0132	11·2	68	0·22
$BaBr_2.H_2O$	0·0086	7·0	31	0·21
$SrBr_2.H_2O$	0·0071	6·3	25	0·37
$BaI_2.H_2O$	0·0029	2·9	0	0·45
$SrI_2.H_2O$	−0·0040	1·1	0	0·61

Notes: $\Delta d = d_{O^i-X(1)^{iii/vii}} - d_{O^i-X(2)^{iv/viii}}$, γ = angle shown in Fig. 4, $\Delta\nu$ = wavenumber difference of the OH stretching modes of HDO molecules present in isotopically dilute samples (Lutz & Christian, 1982), $r_X - r_M$ from Shannon crystal radii (Shannon, 1976).

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