

C(3), C(4) and C(6) and the planes containing atoms C(1), C(2), C(3) and C(4), C(5), C(6) should both be 125.5° . The measured values are respectively 115.0° and 152.9° for this structure and 112.8° and 149.3° for $C_{19}H_{21}Br$. The overall comparison of this structure with the uncomplexed one indicates a small but significant increase in the distortion of the cyclohexane ring.

The chromium atom is calculated to be 1.757 \AA out of the plane of ring *A*. The six individual metal aromatic carbon atom distances differ significantly from one another, the longest distances being those to C(10) and C(15). These are the atoms shared between rings *A* and *B*. A similar situation has also been observed in other structures, e.g. the chromium tricarbonyl naphthalene complex (Kunz & Nowacki, 1967). In this case the chromium-carbon atom distances corresponding to C(7), C(8), C(9), C(10), C(15) and C(16) are respectively 2.191 , 2.219 , 2.214 , 2.337 , 2.306 and 2.186 \AA . The corresponding values in the chromium tricarbonyl phenanthroline complex are 2.210 , 2.206 , 2.208 , 2.289 , 2.289 and 2.212 \AA respectively (Muir & Ferguson, 1968). A check on intermolecular contacts showed that all were 3.50 \AA or greater with the exception of

an $O(1)\cdots O(1)$ contact of 3.22 \AA and an $O(3)\cdots C(13)$ contact of 3.34 \AA .

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References

- CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.
International Tables for X-ray Crystallography (1974). Vol. IV. In the press.
 KUNZ, V. & NOWACKI, W. (1967). *Helv. Chim. Acta*, **50**, 1052–1059.
 MUIR, K. W. & FERGUSON, G. (1968). *J. Chem. Soc. (B)*, pp. 467–476.
 SHAPIRO, B. L., GATTUSO, M. J. & SULLIVAN, G. R. (1971). *Tetrahedron Lett.* pp. 223–226.
 TOWNS, R. L. R., GODWIN, A. D. & SHAPIRO, B. L. (1974). *Cryst. Struct. Commun.* **3**, 31–34.

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The Crystal Structure of Sodium Chloride Dihydrate

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Crystals of $NaCl \cdot 2H_2O$ are monoclinic, probable space group $P2_1/c$, with $a = 6.3313$ (5), $b = 10.1178$ (9), $c = 6.5029$ (6) \AA , $\beta = 114.407$ (7) $^\circ$ and $Z = 4$ at 105 K. 26 of the 'forbidden' reflexions were observed, but a complete structure determination in space group $P2_1/c$ led to an *R* index of 0.0193 and a goodness-of-fit of 2.15 for 2833 reflexions (53 variable parameters). $NaCl \cdot 2H_2O$ is isomorphous with the corresponding bromide. The observed differences between the two structures can be rationalized on the basis of the difference in ionic radii of 0.15 \AA between a bromide and a chloride ion. The electron-density distribution in a water molecule is discussed and the lack of lobes in the electron distribution from the two lone-pair electrons is pointed out.

Introduction

Mitscherlich (1829) (the discoverer of isomorphism) found it easy to grow large single crystals of sodium chloride dihydrate, and he performed the first crystallographic study of this hydrate and the related dihydrates of NaBr and NaI. $NaCl \cdot 2H_2O$ is the only compound formed in the $NaCl-H_2O$ system, and it melts under its own vapour pressure at -0.1°C (Gmelin, 1973). No phase transformation in the solid state has been detected.

The crystal structure of this simple ionic hydrate has never been determined, but it is known to be isomorphous with the corresponding cyanide (Le Bihan, 1958) and bromide, both stable at room temperature. The crystal structure of the bromide was determined by Culot, Piret & Van Meerssche (1962) and independently by Haaf & Carpenter (1964) from X-ray diffraction data. The structure has recently been refined from neutron diffraction data by Tellgren, Pedersen, Tegenfeldt & Olovsson (1974). Sodium iodide dihydrate forms a closely related structure (Verbist, Piret & Van Meerssche, 1970).

Infrared studies by Schiffer & Hornig (1969) and Ford & Falk (1969) and n.m.r. studies by Rockelmann

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& Sillescu (1970) and Håland & Pedersen (1973) show that the static and dynamic structure of sodium chloride dihydrate must be closely similar to that of the bromide. As both salts are key compounds in the understanding of the behaviour of the water molecule under the influence of Coulomb forces, and the chloride is of both biological and geochemical importance, it was decided to determine the structure of this salt. The structure has been determined from three-dimensional X-ray diffraction data from a crystal at 105 K. The data obtained were of high quality, enabling us to determine the atomic positions of all atoms except hydrogen very accurately.

A covalently bound hydrogen atom lacks core electrons and the hydrogen position determined in an X-ray study is known to be systematically shifted from the mean position of its nucleus. As the water molecule is the most complex electronic system in this salt we will discuss the electron distribution in the water molecule in some detail.

Crystal data for NaCl·2H₂O at 105 K are as follows.

$a = 6.3313$ (5) Å	Space group (assumed):
$b = 10.1178$ (9)	$P2_1/c$
$c = 6.5029$ (6)	F.W. 94.47
$\beta = 114.407$ (7)°	$V = 379.34$ Å ³
$\lambda(\text{Mo } K\alpha) = 0.71069$ Å	$Z = 4$
$\mu(\text{Mo } K\alpha) = 9.2$ cm ⁻¹	$D_m(-10^\circ\text{C}) = 1.607$ g cm ⁻³
	(Lindenberg, 1959)
	$D_x = 1.654$ g cm ⁻³

Experimental

Crystals of NaCl·2H₂O were grown by slow evaporation of a saturated solution at -20°C. A crystal cut to an approximately cubic shape (~0.5 mm³) was directly mounted on a Syntex $P\bar{1}$ diffractometer equipped with an Enraf-Nonius gas-flow cooling device, modified by H. Hope. The temperature in the stationary N₂ stream was 105 K at the crystal site. Intensity data were collected using graphite-monochromated Mo $K\alpha$ radiation and the variable ω - 2θ scan speed technique. The reflexion was scanned $\pm 1.5^\circ$ in 2θ about the calculated α_1 and α_2 values. The total time for background counts was 0.7 of the time of integration. The scan speed varied from 2 to 6° (in 2θ) per minute. One quarter of the reciprocal sphere was examined, including absences for the space group $P2_1/c$. In order to reduce ice formation on the specimen, which is most likely to occur at high values of χ , the h index ran through negative values as \mathbf{a}^* was found to be approximately normal to the φ axis of the diffractometer.

The intensities of all reflexions having 2θ less than 45° were measured first. Three standard reflexions were monitored at 40-reflexion intervals. 30 intensities with excessive count rates were re-measured with reduced beam intensity.

The orientation matrix for the crystal was then re-

determined by use of 15 strong reflexions with 2θ between 38 and 45°. The reflexions showed no α_1 - α_2 splitting because of the high crystal mosaicity. The reported cell dimensions with estimated standard deviations were obtained by a least-squares calculation based upon these 2θ values.

The intensities of all reflexions in the 2θ range between 45 and 75° were then measured using a lower limit for registration based on the prescan count rate. The interval between the standard reflexions was increased. Finally the cut-off limit for weak reflexions was readjusted and the intensities of reflexions in the range 75-100° were measured. When about $\frac{2}{3}$ of the data within this shell in reciprocal space had been registered the cooling was accidentally interrupted and the crystal decomposed.

The data collection took one week and some ice formed on the crystal. However, no systematic changes in the standard reflexions were observed. The calculated relative standard deviations for the individual measurements of the three standard reflexions were 0.006, 0.007 and 0.012 respectively, indicating satisfactory experimental conditions and no need for scaling.

2859 independent reflexions were measured with intensity I larger than $3\sigma(I)_{\text{count}}$, where $\sigma(I)_{\text{count}}$ is the estimated standard deviation in the net intensity based on counting statistics. For more than half of the reflexions the ratio $I/\sigma(I)_{\text{count}}$ was greater than 50.

The intensity data were corrected in the usual way by applying Lorentz and polarization factors. A 2% uncertainty due to experimental fluctuations and a count rate correction for non-linearity in the counter were included in the estimated standard deviation in the net intensity [$\sigma^2(I) = \sigma^2(I)_{\text{count}} + (0.02I)^2$]. For the 30 strong reflexions, an additional 2% uncertainty in scaling was also included.

Earlier morphological studies have shown that the crystal is monoclinic and belongs to the point group $2/m$ (Groth, 1906). As pointed out in the Introduction, different experimental methods all indicate that NaCl·2H₂O is isomorphous with NaBr·2H₂O. The space group should therefore be $P2_1/c$ with the following systematic absences: $0k0$ for $k=2n+1$ and $h0l$ for $l=2n+1$. However, 26 of these reflexions were recorded as observed. For 16 reflexions the ratio $I/\sigma(I)_{\text{count}}$ was less than 10. The reflexions -301, -303, -201 and -101 had ratios larger than 20. We will show below that the structure refines satisfactorily in the space group $P2_1/c$ with one formula unit in the asymmetric unit and all atoms in general positions. It therefore seems unlikely that the true space group has lower symmetry than $P2_1/c$. The presence of these reflexions is an interesting aspect of this structure that should be studied further, but we will assume that they can be ignored in the crystal-structure determination.

The accurate shape and orientation of the crystal on the spindle axis had not been measured before the crystal decomposed. A spherical shape ($D=0.45$ mm) was therefore assumed for absorption correction. The

method of Palm (1964) was applied; the transmission factor varied from 0.694 to 0.705.

The computations have been carried out on a CYBER-74 with programs described elsewhere (Groth, 1973). Figures have been prepared by ORTEP (Johnson, 1965). The atomic scattering factors for the heavy atoms have been taken from Doyle & Turner (1968), for hydrogen from Stewart, Davidson & Simpson (1965) and for the valence electrons for oxygen from Harkema (1971). Only real scattering factors have been used.

Structure refinement

The atomic positions found for the bromide (Tellgren *et al.*, 1974) and estimated isotropic temperature factors were used as starting parameters in the full-matrix least-squares refinement. The function minimized was $M = \sum w \Delta F^2$ where $\Delta F = |F_o| - |F_c|$ and $w = 1/\sigma^2(F_o)$. The agreement indices used are $R = \sum |\Delta F| / \sum |F_o|$ and $R_w = (\sum w \Delta F^2 / \sum w F_o^2)^{1/2}$. We give both R and R' where for R the sum is over all allowed reflexions and for R' the sum is only for the reflexions included in the refinement. We also calculate the standard deviation of an observation of unit weight, the so-called goodness-of-fit $S = [\sum w \Delta F^2 / (m - n)]^{1/2}$ where m is the number of reflexions included in the refinement and n the corresponding number of parameters.

The refinement proceeded smoothly and converged (with anisotropic thermal motion for the heavy atoms and isotropic for the hydrogen atoms) to an R_w index of 0.0300 for the 2833 reflexions. R was 0.0193 and increased to 0.0207 when the 26 forbidden reflexions were included. The corresponding difference electron density map based on the 850 reflexions with $\sin \theta/\lambda < 0.65$ contained density fluctuations of $\pm \frac{1}{3} e \text{ \AA}^{-3}$. The atomic parameters obtained and their estimated standard deviations are given in Table 1 and the description of the structure is based on this parameter set. In Table 2 $10F_o$, $10F_c$ and $100\sigma(F_o)$ are listed. 'Forbidden' reflexions are marked with an asterisk.

The weight analysis indicated that systematic errors in the data were present and S was 2.15. Both for weak

reflexions and for the low-angle data the values for $\sum (w \Delta F | \Delta F |) / n_i$ were about equal to the corresponding $\sum w \Delta F^2 / n_i$. There was no indication of extinction effects.

As the number of independent parameters is small, several least-squares refinements on parts of the data were carried out. A summary of these calculations is presented in Table 3. The table clearly shows large changes in the scale factor S_c when low- or high-order data are excluded from the refinement. For all reflexions but two included in refinement V $w \Delta F^2$ was less than 25. For the sodium and chloride ions no significant shifts in position parameters between II and V were observed, all being less than 2σ , whereas for the oxygen atoms shifts up to 5σ occurred. The thermal parameters, however, being highly coupled with the scale factor, showed systematic shifts for all heavy atoms (*cf.* Table 4).

In refinements VI–VIII groups of data for which systematic errors, either experimental or theoretical, may be most important, are omitted. Again, no significant shifts in the position parameters of the heavy atoms were obtained, demonstrating that these positions are probably not influenced by systematic errors in the data.

In the last refinement (IX) the valence-shell electrons of the oxygen atoms and the hydrogen atoms were refined. The parameters for the core electrons of the oxygen atoms and the parameters for the ions were kept constant and equal to the parameters found in refinement V. The agreement was comparable to that of II, but it was difficult to judge whether the model was physically reasonable or not. We then decided to examine the electron density in the regions of the water molecules more closely. In a difference Fourier synthesis based on low-order reflexions ($\sin \theta/\lambda < 0.65$) and parameters from III, no hydrogen atoms could be located. However, a peak at the origin of $1.4 e \text{ \AA}^{-3}$ indicated a systematic error in the scale factor. Several electron density maps were calculated using different scale factors and subtracting the ions and the inner core electrons of the oxygen atoms (parameters from V). To reduce the background noise

Table 1. *Positional and thermal parameters* $\times 10^5$ (*positional parameters for H* $\times 10^3$)

The Debye–Waller factor is $\exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - 2\beta_{12}hk - 2\beta_{13}hl - 2\beta_{23}kl)$. Estimated standard deviations in the last digits are given in parentheses.

	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Na	2374 (4)	17002 (2)	45503 (4)	858 (5)	221 (1)	692 (4)	-29 (4)	715 (8)	3 (4)
Cl	29210 (2)	12190 (1)	21354 (2)	792 (3)	255 (1)	671 (2)	232 (2)	699 (4)	61 (2)
O(1)	78600 (6)	32053 (4)	17284 (7)	831 (7)	259 (2)	913 (7)	66 (6)	610 (13)	33 (7)
O(2)	22780 (6)	49146 (4)	23202 (6)	815 (7)	304 (2)	688 (6)	-111 (7)	511 (12)	110 (6)

Table 1 (*cont.*)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
H(11)	784 (2)	393 (1)	220 (2)	1.3 (2)
H(21)	651 (2)	296 (1)	75 (2)	2.5 (2)
H(12)	361 (2)	520 (1)	251 (2)	1.9 (2)
H(22)	262 (2)	464 (1)	361 (2)	3.6 (3)

only the 388 reflexions with $\sin \theta/\lambda < 0.5$ were included. The scale factor was changed until the electron density in the position of the chloride ion was close to zero ($S_c = 0.0550$). The region about the chloride ion was then flat; at the origin there was a minor bump ($-0.2 e \text{ \AA}^{-3}$) and the electron density at the cation position

Table 2. Observed and calculated structure factors ($\times 10$)

The columns are: $k, l, 10F_o, 10|F_c|$ and $100\sigma(F_o)$. 'Forbidden' reflexions are marked with an asterisk in the third column.

h	k	l	$10F_o$	$10 F_c $	$100\sigma(F_o)$
0	0	0	1000	1000	0
0	0	1	1000	1000	0
0	0	2	1000	1000	0
0	0	3	1000	1000	0
0	0	4	1000	1000	0
0	0	5	1000	1000	0
0	0	6	1000	1000	0
0	0	7	1000	1000	0
0	0	8	1000	1000	0
0	0	9	1000	1000	0
0	0	10	1000	1000	0
0	0	11	1000	1000	0
0	0	12	1000	1000	0
0	0	13	1000	1000	0
0	0	14	1000	1000	0
0	0	15	1000	1000	0
0	0	16	1000	1000	0
0	0	17	1000	1000	0
0	0	18	1000	1000	0
0	0	19	1000	1000	0
0	0	20	1000	1000	0
0	0	21	1000	1000	0
0	0	22	1000	1000	0
0	0	23	1000	1000	0
0	0	24	1000	1000	0
0	0	25	1000	1000	0
0	0	26	1000	1000	0
0	0	27	1000	1000	0
0	0	28	1000	1000	0
0	0	29	1000	1000	0
0	0	30	1000	1000	0
0	0	31	1000	1000	0
0	0	32	1000	1000	0
0	0	33	1000	1000	0
0	0	34	1000	1000	0
0	0	35	1000	1000	0
0	0	36	1000	1000	0
0	0	37	1000	1000	0
0	0	38	1000	1000	0
0	0	39	1000	1000	0
0	0	40	1000	1000	0
0	0	41	1000	1000	0
0	0	42	1000	1000	0
0	0	43	1000	1000	0
0	0	44	1000	1000	0
0	0	45	1000	1000	0
0	0	46	1000	1000	0
0	0	47	1000	1000	0
0	0	48	1000	1000	0
0	0	49	1000	1000	0
0	0	50	1000	1000	0
0	0	51	1000	1000	0
0	0	52	1000	1000	0
0	0	53	1000	1000	0
0	0	54	1000	1000	0
0	0	55	1000	1000	0
0	0	56	1000	1000	0
0	0	57	1000	1000	0
0	0	58	1000	1000	0
0	0	59	1000	1000	0
0	0	60	1000	1000	0
0	0	61	1000	1000	0
0	0	62	1000	1000	0
0	0	63	1000	1000	0
0	0	64	1000	1000	0
0	0	65	1000	1000	0
0	0	66	1000	1000	0
0	0	67	1000	1000	0
0	0	68	1000	1000	0
0	0	69	1000	1000	0
0	0	70	1000	1000	0
0	0	71	1000	1000	0
0	0	72	1000	1000	0
0	0	73	1000	1000	0
0	0	74	1000	1000	0
0	0	75	1000	1000	0
0	0	76	1000	1000	0
0	0	77	1000	1000	0
0	0	78	1000	1000	0
0	0	79	1000	1000	0
0	0	80	1000	1000	0
0	0	81	1000	1000	0
0	0	82	1000	1000	0
0	0	83	1000	1000	0
0	0	84	1000	1000	0
0	0	85	1000	1000	0
0	0	86	1000	1000	0
0	0	87	1000	1000	0
0	0	88	1000	1000	0
0	0	89	1000	1000	0
0	0	90	1000	1000	0
0	0	91	1000	1000	0
0	0	92	1000	1000	0
0	0	93	1000	1000	0
0	0	94	1000	1000	0
0	0	95	1000	1000	0
0	0	96	1000	1000	0
0	0	97	1000	1000	0
0	0	98	1000	1000	0
0	0	99	1000	1000	0
0	0	100	1000	1000	0

Table 2 (cont.)

Table 2 (cont.)

Table with multiple columns of numerical data, likely representing crystallographic parameters or refinement statistics. The data is organized in a grid-like format with various numerical values and some text annotations like "n = 10" or "n = 5".

Table 3. Values of the various agreement indices, defined in the text, obtained in the full-matrix least-squares refinement

Refinement	Atoms refined	Reflexions included	n	m	R	R'	R _w	S _c	S
I	All	All	2833	53	0.0193	0.0193	0.0300	0.0554	2.15
II	All	sin θ/λ < 0.65 F ₀ < 30	800	53	0.0350	0.0158	0.0319	0.0538	2.84
III	Heavy atoms	sin θ/λ > 0.65	1983	37	0.0221	0.0157	0.0224	0.0572	1.44
IV	Heavy atoms	sin θ/λ > 0.75	1566	37	0.0259	0.0164	0.0210	0.0579	1.27
V	Heavy atoms	sin θ/λ > 0.85	1063	37	0.0273	0.0173	0.0205	0.0581	1.14
VI	All	sin θ/λ > 0.40 4 < F ₀ < 16	1493	53	0.0193	0.0118	0.0184	0.0563	1.51
VII	All	sin θ/λ > 0.40 2 < F ₀ < 16	2163	53	0.0195	0.0152	0.0234	0.0561	1.68
VIII	All	sin θ/λ > 0.40 1 < F ₀ < 16	2436	53	0.0197	0.0177	0.0271	0.0561	1.83
IX	H atoms and valence shell for O	sin θ/λ < 0.65	850	35	0.0293	0.0217	0.0346	0.0561	2.88

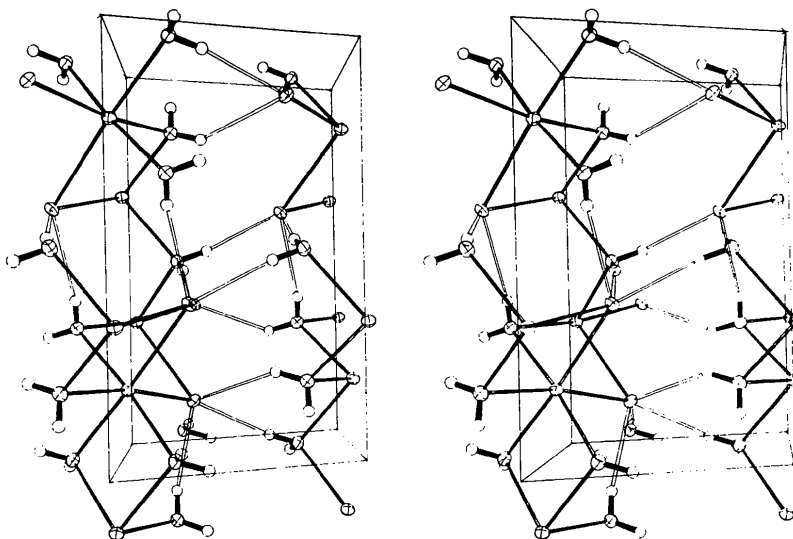


Fig. 1. A stereoscopic illustration of the structure seen along [001]. The thermal vibration ellipsoids of the non-hydrogen atoms are 50% probability surfaces. The b axis is vertical.

Table 4. The root-mean-square amplitude of the atoms along the three principal axes, and the components of the unit vectors along the principal axes referred to the crystallographic axes ($\times 10^4$)

Refinement	Atom	R. m. s. amplitude (Å)	B	e_x	e_y	e_z
I	Na ⁺	0.121	1.15	1716	-130	794
		0.109	0.93	30	549	1292
		0.106	0.89	254	813	-746
	Cl ⁻	0.129	1.32	1236	694	509
		0.107	0.91	528	-315	1594
		0.097	0.75	-1098	630	236
	O(1)	0.131	1.36	299	18	-1395
		0.121	1.16	1344	609	766
		0.112	1.00	1056	-779	568
	O(2)	0.135	1.45	-730	753	465
		0.113	1.01	1530	465	656
		0.107	0.91	369	-441	1486
II	Na ⁺	0.127	1.26	1712	-157	734
		0.116	1.05	58	375	1446
		0.114	1.03	274	902	-474
	Cl ⁻	0.135	1.43	1206	710	420
		0.113	1.01	413	-172	1636
		0.103	0.85	1178	-667	27
	O(1)	0.143	1.61	482	216	-1246
		0.121	1.16	1584	241	1141
		0.119	1.11	519	-935	6
	O(2)	0.144	1.65	-591	805	487
		0.120	1.14	1466	480	242
		0.113	1.01	716	-317	1600
V	Na ⁺	0.116	1.07	1719	-133	721
		0.105	0.87	128	641	1218
		0.102	0.83	198	742	-923
	Cl ⁻	0.126	1.25	1225	701	495
		0.104	0.85	511	-292	1604
		0.094	0.69	-1119	634	191
	O(1)	0.127	1.27	-177	77	1454
		0.119	1.11	1315	645	571
		0.108	0.92	1118	-746	643
	O(2)	0.130	1.34	-722	720	548
		0.108	0.93	1375	578	284
		0.104	0.85	774	-355	1573

was also close to zero ($-0.2 e \text{ \AA}^{-3}$), but with a slight gradient. Sections through the water molecules in this difference map are given in Fig. 3 and will be discussed below. The sections may be distorted by systematic errors in the intensities, whereas phase errors should be of no importance.

Description of the structure

The final positional and thermal parameters for all atoms are given in Table 1. The estimated standard deviations in the coordinates for the heavier atoms are a factor of ten better than those obtained in the neutron diffraction study of the bromide (Tellgren *et al.*, 1974). However, both determinations are accurate enough to give a sufficiently detailed picture of the

structure. It has to be remembered when comparing the two structures that they have been determined at different temperatures. The thermal expansion of these salts is not known, but if it is about equal to that of the anhydrous salts then differences given in Table 5 of about 0.02 Å might be due to the temperature difference (Pautamo, 1963).

Table 5. Interatomic distances (Å) in NaCl·2H₂O (at 105 K) and the difference, Δ , between a distance in this salt and the corresponding distance in NaBr·2H₂O (at 298 K)

The positions of the first atoms are as given in Table 1. The positions of the second atoms are given in terms of the coordinates in Table 1. Uncertainty in the cell constants has been included in the standard deviations.

	Position of second atom		$\Delta \times 10^3$ (Å)
Na—O(2)	$(x, \frac{1}{2}-y, \frac{1}{2}+z)$	2.3789 (4)	-26
Na—O(2')	$(-x, -\frac{1}{2}+y, \frac{1}{2}-z)$	2.3829 (5)	-24
Na—O(1)	$(-1+x, y, z)$	2.3810 (4)	-34
Na—O(1')	$(-1+x, \frac{1}{2}-y, \frac{1}{2}+z)$	2.4582 (4)	-37
Na—Cl	(x, y, z)	2.7919 (3)	-173
Na—Cl'	$(x, \frac{1}{2}-y, \frac{1}{2}+z)$	2.7901 (3)	-181
O(1)—Cl	$(1-x, \frac{1}{2}+y, \frac{1}{2}-z)$	3.2234 (5)	-163
O(1)—Cl'	$(x, \frac{1}{2}-y, -\frac{1}{2}+z)$	3.3644 (5)	-222
O(2)—Cl	$(x, \frac{1}{2}-y, \frac{1}{2}+z)$	3.1990 (4)	-167
O(2)—Cl'	$(1-x, \frac{1}{2}+y, \frac{1}{2}-z)$	3.1964 (4)	-143
O(1)—H(11)	(x, y, z)	0.79 (1)	170
O(1)—H(21)	(x, y, z)	0.87 (1)	70
O(2)—H(12)	(x, y, z)	0.85 (1)	110
O(2)—H(22)	(x, y, z)	0.83 (1)	130

A general view of the structure is shown in Fig. 1. Essential building blocks in the structure are the octahedra about each sodium ion shown in Fig. 2 and the tetrahedra about each water molecule. The structure consists of interconnected sodium octahedra sharing edges forming layers parallel to the (100) plane similar to the packing in gibbsite (Wells, 1962). The layers are connected by hydrogen bonds. The bonding is therefore very anisotropic, thus explaining the easy cleavage of the crystal along (100).

The sodium ions form an approximately hexagonal net parallel to (100). The shortest Na—Na distances in the chloride are 3.523 and 3.632 Å and in the bromide

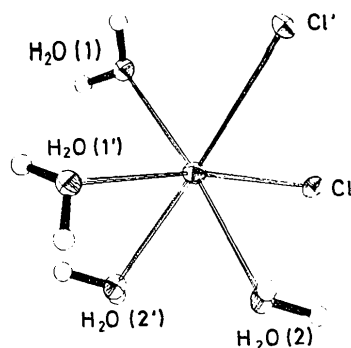


Fig. 2. The coordination about the sodium ion.

3.595 and 3.791 Å. This is much shorter than in the dehydrated salts where the shortest Na–Na distance is respectively 5.640 and 5.978 Å. On the other hand the Na–Cl distances given in Table 5 are only slightly smaller than the Na–Cl distance in NaCl at the same temperature, 2.800 Å. This indicates that the water–anion repulsion must be as strong as the anion–anion repulsion in the anhydrous salts. As shown by Bush & Truter (1971), if the oxygen ligands about sodium move out then the Na–Br distance gets shorter [2.82 (1) Å in their case compared to 2.98 Å in NaBr]. The anion–water repulsion also makes the Na–O distances somewhat longer here than observed in cases where sodium is solely coordinated to oxygen atoms (Truter, 1973).

The difference between the shortest Na–anion dis-

tance in NaCl at 105 K and NaBr at room temperature is -0.177 Å. The Goldsmith ionic radius for Cl^- is 1.81 Å, and for Br^- 1.96 Å, a difference of -0.15 Å. Remembering the uncertainty due to the temperature difference all changes in the distances given in Table 5 in going from the bromide to the chloride can be understood simply as a size effect. The largest change is observed in the longest $\text{O}(1)\cdots$ anion distance, but this distance is also probably the 'softest' so the thermal change in this bond might be large.

The observed angular deformations in the octahedron about sodium can also be understood as an effect resulting from packing two larger halide ions and four smaller water oxygens about each sodium ion. The angles are given in Table 6 together with a comparison with the corresponding angles in the bromide.

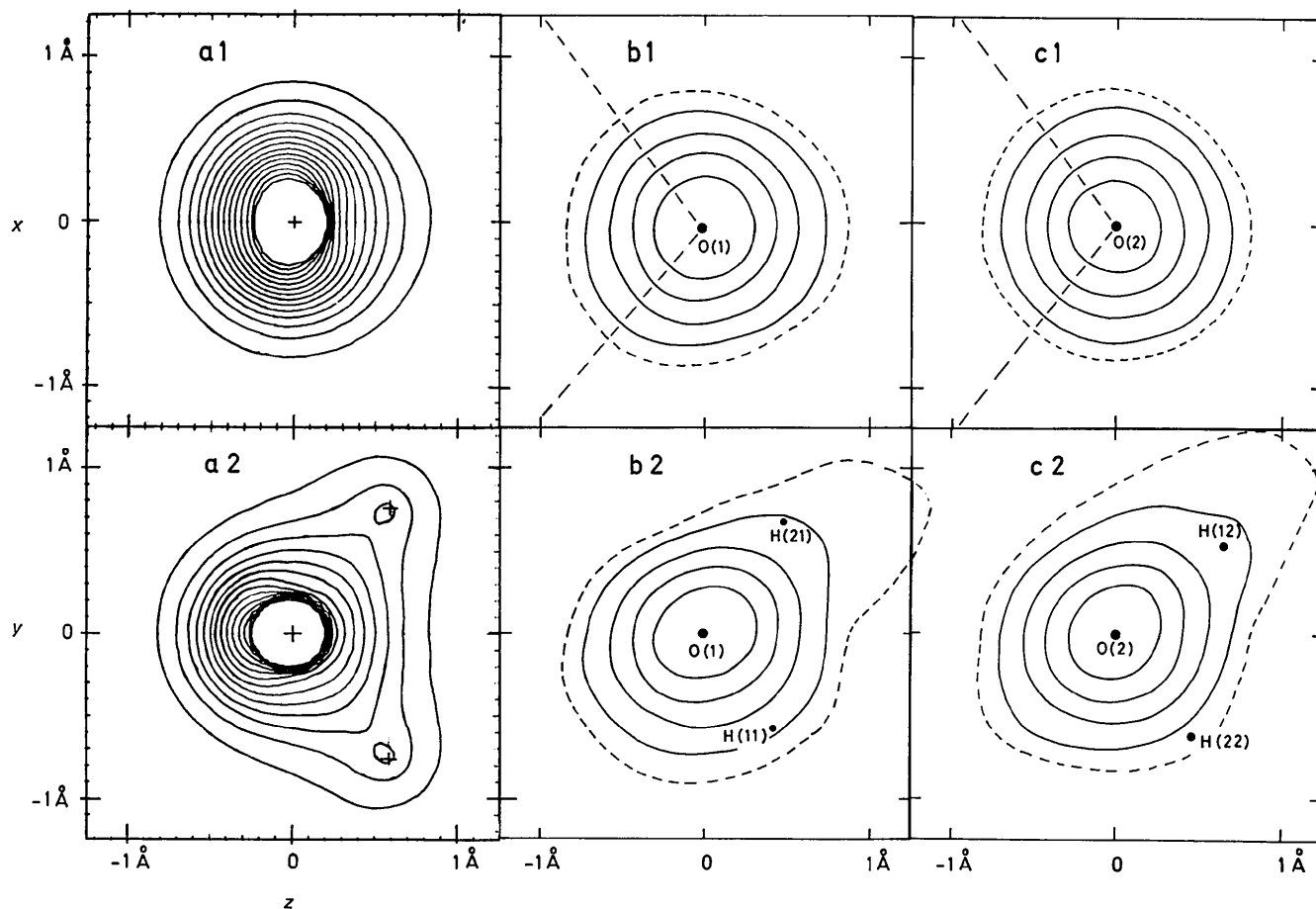


Fig. 3. Sections of the electron density through the water molecule. The two sections to the left, *a1* and *a2*, are theoretical electron densities from an *ab initio* calculation by Pitzer & Merrifield (1970). *a1* is the section in the molecular plane (*yz* plane). *a2* is the section orthogonal to the molecular plane cutting the molecular plane along the twofold axis of the molecule (the *z* axis). The positions of the atomic nuclei are marked with crosses. The other sections are analogous experimental sections through the observed electron density of $\text{H}_2\text{O}(1)$ and $\text{H}_2\text{O}(2)$ with the inner core (*1s*) electrons on the oxygen atoms subtracted. *b2* and *c2* are sections in the molecular plane. *b1* and *c1* are sections in the Na–O–Na planes which are approximately orthogonal to the molecular plane and cutting the molecular plane approximately along the bisector of the H–O–H angle. The broken straight lines indicate the directions to the neighbouring sodium ions. The contours on the theoretical maps are at $\frac{1}{3} e \text{ \AA}^{-3}$ intervals starting from $\frac{1}{3} e \text{ \AA}^{-3}$. Those in the experimental maps are at $1 e \text{ \AA}^{-3}$ intervals starting from $1 e \text{ \AA}^{-3}$. The broken contour on the experimental maps is the $0.5 e \text{ \AA}^{-3}$ contour.

Table 6. *Angles in the octahedron about Na in NaCl.2H₂O (at 105 K) and the difference, Δ, between an angle in this salt and the corresponding angle in NaBr.2H₂O (at 298°K)*

The estimated standard deviation in an angle is 0.01–0.02°. The atomic positions are given in Table 5.

		Δ
Cl—Na—Cl'	96.31°	2.0°
Cl—Na—O(1)	90.87	1.2
Cl—Na—O(1')	172.18	-1.8
Cl—Na—O(2)	92.28	1.5
Cl—Na—O(2')	90.83	0.9
Cl'—Na—O(1)	90.88	-1.2
Cl'—Na—O(1')	89.36	0.9
Cl'—Na—O(2)	93.27	0.2
Cl'—Na—O(2')	172.63	-1.8
O(1)—Na—O(1')	94.39	-1.1
O(1)—Na—O(2)	174.46	-0.3
O(1)—Na—O(2')	90.87	-0.6
O(1')—Na—O(2)	81.99	-1.7
O(1')—Na—O(2')	83.36	-3.6
O(2)—Na—O(2')	84.55	1.3

The coordination about the water molecules is tetrahedral and closely similar to that observed in the bromide. As the so-called hydrogen atom positions are systematically shifted away from the position of the nucleus (determined in the neutron study) a look at the description of the hydrogen bonding in Tellgren, *et al.* (1974) is recommended. The lengths of the O—Cl hydrogen bonds have been predicted by Schiffer & Hornig (1969) from infrared spectra at 80 K. The predicted value of the longest bond is close to the observed value, but the shorter bonds are observed 0.04 to 0.07 Å shorter than predicted.

The electron distribution in the water molecules

It is clear from the refinement that the experimental data show that the structure consists of sodium and chloride ions and water molecules. Apparently the description of the ions as spherically symmetric 10- and 18-electron atoms vibrating harmonically about their mean positions is a good model. In Table 4 the principal r.m.s. amplitudes and the directions of the principal axes for the heavy atoms are given. From these data it follows that the motion is nearly isotropic. The mean-square amplitudes are about $\frac{1}{3}$ of the corresponding amplitudes in the bromide (Haaf & Carpenter, 1964; Tellgren *et al.*, 1974). This reduction is reasonable as the chloride structure was determined at $\frac{1}{3}$ of the absolute temperature of the bromide.

The distribution of the ten electrons in each of the two crystallographically independent water molecules is not spherically symmetric. This is the basic reason why the position of the oxygen atoms shifted when the refinement was carried out on the high-angle data. In the high-angle data it will be the scattering from the core electrons on oxygen that dominates and the contribution from the valence electrons will be negligible.

In Fig. 3 sections through the electron distribution in H₂O(1) and H₂O(2) calculated from the low-angle data are given. The theoretical electron density from an *ab initio* calculation by Pitzer & Merrifield (1970) is also given. We can see that the calculated and experimental electron densities are similar. The experimental sections are somewhat blurred from noise and from the mainly zero-point motion of the molecule.

The most significant aspect, in our opinion, of these electron density maps for the crystal chemistry of hydrates is the complete lack of individual lone-pair orbitals. The popular view of the electron distribution in a water molecule is a methane-like molecule with two of the protons displaced towards the carbon nucleus. The water molecule is therefore regarded as consisting of four tetrahedral *sp*³ orbitals, two bonding two hydrogen atoms and two lone-pair orbitals sticking out like a rabbit's ears. This picture has been used by Chidambaram, Sequeira & Sikka (1964) as the basis of a classification of water molecules in hydrates, and the directional influence of the lone-pairs on the hydrogen-bond geometry has also been much discussed (Donohue, 1968). The electron distributions shown here are more like what one would get by gluing together one half of a methane molecule and one half of a fluoride ion. One should also remember that two quite different lone-pair orbitals are used in discussing the electronic spectra of a water molecule: one *p* orbital and the other more like an *sp* orbital. The energy difference between the two orbitals is about 50 kcal mole⁻¹ (Dunning, Pitzer & Aung, 1972; Jorgensen & Salem, 1973). However, an orbital is not an observable but a quantity only defined within the framework of an approximation. The molecular electron density, on the other hand, is an observable quantity. It is therefore significant when neither the theoretical nor the experimental electron density maps show any concentration of electric charge in the lone-pair regions. One should also expect that the interaction with the cations should enhance any such concentration in the experimental maps.

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References

- BUSH, M. A. & TRUTER, M. R. (1971). *J. Chem. Soc. B*, pp. 1440–1446.
 CHIDAMBARAM, R., SEQUEIRA, A. & SIKKA, S. K. (1964). *J. Chem. Phys.* **41**, 3616–3622.
 CULOT, J. P., PIRET, P. & VAN MEERSSCHE, M. (1962). *Bull. Soc. Fr. Minér. Crist.* **85**, 282–289.
 DONOHUE, J. (1968). In *Structural Chemistry and Molecular Biology*, edited by A. RICH and N. DAVIDSON. San Francisco: Freeman.
 DOYLE, P. A. & TURNER, P. S. (1968). *Acta Cryst.* **A24**, 390–397.

- DUNNING, T. H. JR, PITZER, R. M. & AUNG, S. (1972). *J. Chem. Phys.* **57**, 5044–5051.
- FORD, T. A. & FALK, M. (1969). *J. Mol. Struct.* **3**, 445–452.
- GMELIN (1973). *Handbuch der anorganischen Chemie*. System 21, *Natrium*. Weinheim: Verlag Chemie.
- GROTH, P. (1906). *Chemische Kristallographie*, Teil 1, p. 233. Leipzig: Engelmann.
- GROTH, P. A. (1973). *Acta Chem. Scand.* **27**, 1837.
- HAAF, W. R. & CARPENTER, G. B. (1964). *Acta Cryst.* **17**, 730–732.
- HARKEMA, S. (1971). *Thesis*, Technische Hogeschool Twente, Netherlands.
- HÅLAND, K. & PEDERSEN, B. (1973). *J. Chem. Phys.* **58**, 3472–3485.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- JORGENSEN, W. L. & SALEM, L. (1973). *The Organic Chemist's Book of Orbitals*. New York: Academic Press.
- LE BIHAN, M. T. (1958). *Acta Cryst.* **11**, 770–773.
- LINDENBERG, W. (1959). *Z. anorg. allgem. Chem.* **299**, 203–212.
- MITSCHERLICH, E. (1829). *Ann. Phys. Lpz.* **17**, 385–388.
- PALM, J. H. (1964). *Acta Cryst.* **17**, 1326–1327.
- PAUTAMO, Y. (1963). *Ann. Acad. Sci. Fenn. A VI*, **129**, 1–45.
- PITZER, R. M. & MERRIFIELD, D. P. (1970). *J. Chem. Phys.* **52**, 4782–4787.
- ROCKELMANN, V. H. & SILLESCU, H. (1970). *Ber. Bunsenges. Phys. Chem.* **74**, 999–1002.
- SCHIFFER, J. & HORNIG, D. F. (1969). U.S. Natl. Bur. Stand. *Spec. Publ.* 1967, No. 301, 257–259.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
- TELLGREN, R., PEDERSEN, B., TEGENFELDT, J. & OLOVSSON, I. (1974). *Hydrogen Bond Studies. Neutron Diffraction Study of Sodium Bromide Dihydrate*. To be published.
- TRUTER, M. R. (1973). *Struct. Bond.* **16**, 71–111.
- VERBIST, J., PIRET, P. & VAN MEERSSCHE, M. (1970). *Bull. Soc. Fr. Minér. Cryst.* **93**, 509–514.
- WELLS, A. F. (1962). *Structural Inorganic Chemistry*. Oxford Univ. Press.

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A Constrained Refinement of the Structure of Durene Including 'Wagging' Vibrations of the Methyl Groups

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It has been possible to improve a previous constrained refinement of durene based on a procedure relating the second and third cumulant coefficients in the structure-factor formula to the molecular motion parameters. The improvement results from two factors. First, the use of a temperature-factor expression which is better adapted to great librational amplitudes, gave a weighted R of 0.095 instead of 0.115 in the previous analysis, without using additional parameters. Secondly, the inclusion of wagging vibrations reduced the weighted R to 0.086. For a methyl group and the corresponding ring atom, wagging is described as a libration about an axis lying in the ring plane and perpendicular to the single bond. A displacement of the wagging centre on the single bond strongly modifies the values of some external and internal libration tensors, even though the R value is almost insensitive to this displacement. A reasonable mechanistic model has been chosen on the basis of the best agreement between spectroscopic frequencies and frequencies calculated from libration tensors. The wagging centre is a distance of 0.69 Å from the carbon atom of the ring. The average wagging tensor is $55.7(\text{°})^2$. The unusual result that the Raman frequency of libration around the OY axis (103 cm^{-1}) is considerably higher than that around the OX axis (72 cm^{-1}), even though the moment of inertia around OY is twice that around OX , is very well confirmed in a refinement including wagging, the calculated frequencies from librational tensor being respectively 130 and 50 cm^{-1} .

Introduction

Recently, Prince & Finger (1973) have described a procedure applicable to centrosymmetric rigid molecules for refining directly the usual rigid-body parameters L_{ij} and T_{ij} , and the librational tensor θ of side groups free to librate around a single bond. This treatment, which generalizes Johnson's (1970*a, b*) procedure for relating the second and third cumulant coefficients in the structure-factor formula to the molecular motion parameters, has been applied to a refinement of the

structure of durene from neutron diffraction data (Prince, Schroeder & Rush, 1973). The test using the R -factor ratio (Hamilton, 1965) shows that a conventional unconstrained refinement gives a significantly better fit to the data than does the constrained one. On the other hand, the usual unrestrained model gives some positional and thermal parameters which are physically unreasonable. Those obtained in the restrained model have more physical significance. However, Prince *et al.*, when they compare librational and torsional frequencies of durene derived from their