

displaced by one octahedron diagonal with respect to each other. This linkage is the same as that occurring in one of the Nb_2O_5 modifications, namely $N\text{-Nb}_2\text{O}_5$ (Andersson, 1967b).

In conclusion we note that electron diffraction and crystal structure imaging techniques have been of paramount importance in the deduction of a plausible structure of $\text{NaNb}_7\text{O}_{18}$. These results will serve as a good starting point for a more accurate structure determination, should X-ray single-crystal diffraction data become available in the future. We also think that continued studies using HREM of $\text{NaNb}_7\text{O}_{18}$ or similar compounds will reveal further types of structural defects. Such work is now under way.

We wish to express our thanks to Professor Lars Kihlberg for his continuous interest in this work

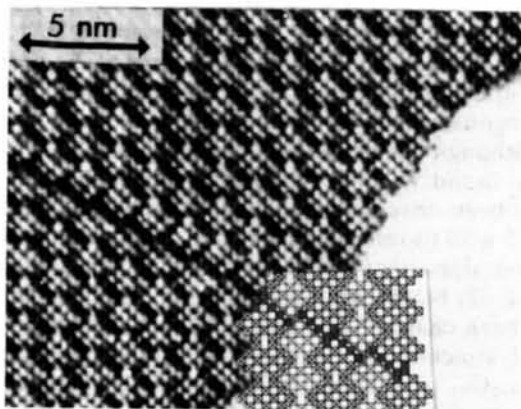


Fig. 6. HREM image of a thin crystal flake illustrating a second type of defect observed in $\text{NaNb}_7\text{O}_{18}$. An interpretation is inserted.

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A Crystal Chemical Study of the System $\text{CsCl-NaCl-H}_2\text{O}$; Structures of the CsCl Derivative Compounds $\text{Cs}_{1-x}(\text{Na}\cdot\text{H}_2\text{O})_x\text{Cl}$, $\text{CsNa}_2\text{Cl}_3\cdot 2\text{H}_2\text{O}$, and $\text{Cs}_2\text{CaCl}_4\cdot 2\text{H}_2\text{O}$

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Abstract

A restudy of the system $\text{CsCl-NaCl-H}_2\text{O}$ {previously described by Plyushchev, Tulinova, Kutznetsova, Korovin & Petrova [*Zh. Neorg. Khim.* (1957). 2, 2212–2220; *J. Inorg. Chem. USSR* (1957). 2, 357–368]} yielded a new compound, which was found by crystal

and comments on the manuscript. We are also grateful to Mrs Gunvor Winlöf for skilful technical assistance. The present study has been performed within a research program supported by the Swedish Natural Science Research Council. A grant from the Knut and Alice Wallenberg Foundation for the JEOL 200 CX electron microscope is gratefully acknowledged.

References

- ALLPRESS, J. G. & SANDERS, J. V. (1973). *J. Appl. Cryst.* 6, 165–190.
ANDERSSON, S. (1965a). *Acta Chem. Scand.* 19, 557–563.
ANDERSSON, S. (1965b). *Acta Chem. Scand.* 19, 2285–2290.
ANDERSSON, S. (1965c). *Bull. Soc. Chim. Fr.* pp. 1088–1094.
ANDERSSON, S. (1967a). *Acta Chem. Scand.* 21, 1777–1782.
ANDERSSON, S. (1967b). *Z. Anorg. Allg. Chem.* 351, 106–112.
APPENDINO, P. (1973). *Annal. Chim. (Rome)*, 63, 547–556.
BRUSSET, H., GILLIER-PANDRAUD, H. & BELLE, J.-P. (1967). *Bull. Soc. Chim. Fr.* pp. 2276–2283.
COWLEY, J. M. & MOODIE, A. F. (1957). *Acta Cryst.* 10, 609–619.
GOODMAN, P. & MOODIE, A. F. (1974). *Acta Cryst.* A30, 280–290.
HAMBLING, P. G. (1953). *Acta Cryst.* 6, 98.
HÖRLIN, T., MARINDER, B.-O. & NYGREN, M. (1982). *Rev. Chim. Minér.* 19, 231–238.
IJIMA, S. (1973). *Acta Cryst.* A29, 18–24.
JOHANSSON, K. E., PALM, T. & WERNER, P.-E. (1980). *J. Phys. E*, 13, 1289–1291.
MARINDER, B.-O. (1983). In preparation.
MARINDER, B.-O. & SUNDBERG, M. (1982). *Proc. R. Microsc. Soc.* 17, 38.
SHAFFER, M. W. & ROY, R. (1959). *J. Am. Ceram. Soc.* 42, 482–486.
SHELDRIK, G. M. (1976). *SHELX*. A program for crystal structure determination. Univ. of Cambridge, England.
SKARNULIS, A. J., LILJESTRAND, G. & KIHILBORG, L. (1979). *Chem. Commun. Univ. Stockholm*, No. 1.
SMITH, G. S. & SNYDER, R. L. (1979). *J. Appl. Cryst.* 12, 60–65.
SUNDBERG, M. & MARINDER, B.-O. (1983). In preparation.
WERNER, P.-E. (1969). *Ark. Kemi*, 31, 513–516.
YVON, K., JEITSCHKO, W. & PARTHÉ, E. (1977). *J. Appl. Cryst.* 10, 73–74.

for 1135 independent reflections [$I > 2\sigma(I)$]. The structure consists of a slightly distorted cubic CsCl framework in which $\frac{2}{3}$ of the Cs atoms are replaced by H_2O molecules and Na atoms inserted in cubic Cl_4 face centers between pairs of H_2O molecules, forming coiled $(\text{Na}\cdot\text{H}_2\text{O})_n$ chains. This structural principle was found to account for the existence of the unusual solid-solution series $\text{Cs}_{1-x}(\text{Na}\cdot\text{H}_2\text{O})_x\text{Cl}$, in which x can range from 0 to 0.43 at 298 K. These solid solutions contain H_2O replacing Cs, with $(\text{Na}\cdot\text{H}_2\text{O})_n$ chains looped or coiled at random in the cubic structure. It was found that Ca behaves with H_2O in a similar manner in the previously known compound $\text{Cs}_2\text{CaCl}_4\cdot 2\text{H}_2\text{O}$. Crystals ($M_r = 483.73$) are triclinic, space group $P\bar{1}$, with cell dimensions (from Guinier-Hagg powder refinement) $a = 6.9038$ (7), $b = 7.5127$ (9), $c = 5.8774$ (7) Å, $\alpha = 92.28$ (1), $\beta = 96.19$ (1), $\gamma = 65.23$ (1)°, $V = 275.17$ (4) Å³ ($= 4 \times 68.8$ Å³), $Z = 1$, $D_x = 2.919$, D_m (Berman balance) = 2.89 (2) g cm⁻³, $\text{Mo K}\alpha$, $\mu = 75.5$ cm⁻¹, $F(000) = 218$, $R = 0.079$ for 1477 independent reflections [$I > 2\sigma(I)$]. The structure is similar in principle to that of the Na compound, but discrete H_2O -Ca- H_2O groups are formed, isolated from each other. $\text{Cs}_2\text{CaCl}_4\cdot 2\text{H}_2\text{O}$ is isostructural with $\text{Cs}_2\text{MnCl}_4\cdot 2\text{H}_2\text{O}$ and $\text{Rb}_2\text{MnCl}_4\cdot 2\text{H}_2\text{O}$. (The JCPDS Diffraction File Nos. for $\text{CsNa}_2\text{Cl}_3\cdot 2\text{H}_2\text{O}$ and $\text{Cs}_2\text{CaCl}_4\cdot 2\text{H}_2\text{O}$ are: 34-1489 and 34-1490).

Introduction

The behavior of cesium in salt brines has become of considerable interest in connection with the proposed disposal of high-level radioactive wastes containing ¹³⁷Cs ($t_{1/2} = 30$ y) in deep salt deposits. To broaden our knowledge of the influence of Cs on such brine systems, we have undertaken a detailed study of the system CsCl - NaCl - H_2O . A previous study has been carried out and reported by Plyushchev, Tulinova, Kutznetsova, Korovin & Petrova (1957), but we have refined their work and revealed important new features. These include the discovery of the previously unsuspected compound $\text{CsCl}\cdot 2\text{NaCl}\cdot 2\text{H}_2\text{O}$, and the determination that the (Cs, Na)Cl solid solution reported by Plyushchev *et al.* contains water according to the formulation $\text{Cs}_{1-x}(\text{Na}\cdot\text{H}_2\text{O})_x\text{Cl}$.

As described by Chou, Romankiw, Evans & Konnert (1983), the solubility relationships in the ternary system CsCl - NaCl - H_2O were measured at 298 K by visual polythermal and isothermal techniques in order to refine the results of Plyushchev, Tulinova, Kutznetsova, Korovin & Petrova (1957). The ternary diagram at 298 K based on the data of the latter authors is shown in Fig. 1. Two solid phases reported by Plyushchev *et al.* were: pure NaCl, containing no measurable dissolved CsCl; and CsCl, which apparently can incorporate more than 30 mol % NaCl in solid solution. The last observation is unexpected, because

in the binary system NaCl - CsCl , measured and described by Zemczuzny & Rambach (1910), no detectable solid solution was found in either end member. Nevertheless, when we investigated this region of the system, we found that the tie lines did apparently extend to the NaCl - CsCl axis up to 43 mol %.

At the end of the solid-solution series, in a narrow solution composition range (within $\pm 1\%$), there appeared large prismatic crystals of a wholly new phase. The colorless crystals decomposed in air within a few days, apparently through loss of water of crystallization. By crystal structure analysis, described below, the composition was determined to be $\text{CsCl}\cdot 2\text{NaCl}\cdot 2\text{H}_2\text{O}$, or $\text{CsNa}_2\text{Cl}_3\cdot 2\text{H}_2\text{O}$. This result suggested that if the solid-solution phases near CsCl actually contained H_2O in addition to NaCl, the peculiar properties of these phases would be accounted for. In fact, chemical analysis of carefully dried samples in the solid-solution range revealed that H_2O is present in an amount equimolar to NaCl. Thus, it is found that CsCl and NaCl in the presence of H_2O extensively interact with each other.

Fig. 2 shows the CsCl - NaCl - H_2O system at 298 K as revised by our studies: the physical chemical studies in the range 293-393 K by Chou & Lee (1983), and by Chou & Romankiw (1983); and the crystal chemical studies at 298 K described in this paper, and by Chou, Romankiw, Evans & Konnert (1983). The crystal chemical aspects of the study, namely, the crystal structure study of the new compound $\text{CsNa}_2\text{Cl}_3\cdot 2\text{H}_2\text{O}$ and the solid-solution series $\text{Cs}_{1-x}(\text{Na}\cdot\text{H}_2\text{O})_x\text{Cl}$, are described in this paper. The crystal structure of the related compound $\text{Cs}_2\text{CaCl}_4\cdot 2\text{H}_2\text{O}$ is also presented. Preliminary reports have appeared as abstracts (Chou, Romankiw, Evans & Konnert, 1982; Evans, Konnert, Chou & Romankiw, 1982).

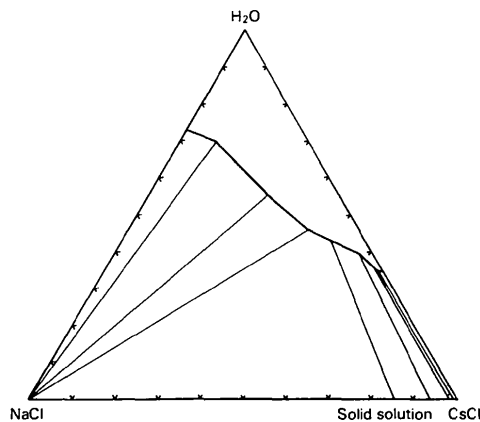


Fig. 1. The CsCl - NaCl - H_2O system as determined by Plyushchev, Tulinova, Kutznetsova, Korovin & Petrova (1957). Graduations are in wt %.

Experimental procedures

The techniques for preparing and treating solutions and crystals are described by Chou & Lee (1983), Chou & Romankiw (1983) and Chou *et al.* (1983). Crystals containing CsCl tend to be hygroscopic, and in high humidity may convert to a liquid. Generally, samples could be prepared for X-ray powder study in air, but for single-crystal study it was necessary to enclose the crystal together with a drop of mother liquor in thin-walled glass capillary tubes.

Powder patterns were prepared with the Guinier–Hägg technique, using Cu K α_1 radiation ($\lambda = 1.54052 \text{ \AA}$) and an internal standard (CaF₂, $a = 5.4638 \text{ \AA}$). These provided the data for the refinement by least-squares analysis of unit-cell parameters given in the *Abstract*.

For structure analysis, X-ray intensities were measured on an automated Picker four-circle single-crystal diffractometer. For this study, no problems of diffuse or irregular reflection profiles were encountered, and reflections were scanned in a θ – 2θ mode, bracketing the α doublet by 1° on either side. Nb-filtered Mo K α radiation was used, and a standard reflection monitored about once an hour. The conditions of data measurement and structure refinements of CsNa₂Cl₃·2H₂O and Cs₂CaCl₄·2H₂O are given in Tables 1 and 4, respectively. The isotropic extinction parameter was refined concurrently with the structure refinements. All calculations were carried out with the XRAY76 program system (Stewart, 1976). Scattering factors for Cs⁺, Na⁺, Ca²⁺, Cl[–] and O[–] were taken from the exponential forms given by Cromer & Mann (1968).

Cesium disodium trichloride dihydrate

Large, colorless, prismatic crystals, usually occurring as penetration twins with composition planes (100) and (001), form readily at 298 K from solutions containing CsCl and NaCl in the molar ratio of 1:38:1

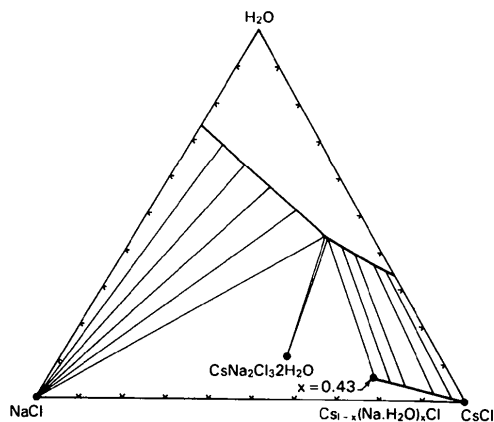


Fig. 2. The revised CsCl–NaCl–H₂O phase diagram as determined by Chou *et al.* (1983). Graduations are in wt %.

Table 1. *Experimental details for CsNa₂Cl₃·2H₂O*

Crystal size:	0.14 × 0.10 × 0.4 mm
Corrections:	Lorentz, polarization, absorption, dispersion, isotropic extinction
Reflections measured:	~2500; 1206 independent with $2\theta < 60^\circ$ (Mo K α radiation)
Reflections used for refinement:	1135 with $I > 2\sigma(I)$; weights $w = 1/\sigma^2$ (from counting statistics)
Refinement:	42 variables; to $R = 0.022$, $R_w = 0.024$
$(\Delta/\sigma)_{\max}$:	0.001

Table 2. *Structure parameters and root-mean-square thermal motions of atoms in CsNa₂Cl₃·2H₂O*

$$\bar{u}^2 = \frac{1}{3} \sum_i U_{ii}$$

	x	y	z	\bar{u} (Å)
Cs	0.25	0.25	0.25	0.177 (1)
Na(1)	0	0	0	0.172 (4)
Na(2)	0	0.6652 (2)	0.25	0.171 (4)
Cl(1)	0.15861 (3)	0.26673 (10)	0.58579 (5)	0.168 (2)
Cl(2)	0	0.18249 (14)	0.25	0.164 (2)
O	0.3941 (1)	0.2049 (3)	0.5741 (2)	0.170 (4)
H(1)	0.326 (3)	0.250 (10)	0.580 (4)	0.17 (3)
H(2)*	0.385 (3)	0.073 (7)	0.519 (4)	0.22 (5)

* Coordinates from difference map.

(the saturated solution contains 98.4 g CsCl and 24.8 g NaCl in 100 g H₂O). The crystals are monoclinic, and were found by systematic extinctions on single-crystal precession photographs to belong to the space group $I2/c$ or Ic . The unit-cell parameters given in the *Abstract* were refined by least-squares analysis of X-ray powder data obtained with the Guinier–Hägg focusing camera [for 58 reflections, $\sigma(2\theta) = 0.014^\circ$]. The powder data have been deposited.*

The crystal structure was solved in $I2/c$ by the symbolic addition procedure. Initial interpretation of the result was hampered by the assumption of a false composition based on an incorrect density determination made on impure material (crystals were contaminated by overgrowths of the cubic solid solution phase). As soon as the nonhydrogen atoms were all correctly identified, the refinement (on F) converged rapidly and satisfactorily to $R = 0.036$. The assumed centrosymmetric space group was thus confirmed. When absorption corrections were recalculated using the proper absorption parameter ($\mu = 50.0 \text{ cm}^{-1}$), the final refinement reached $R = 0.023$. The composition of the compound determined in this way was subsequently confirmed by chemical analysis of pure material (Chou *et al.*, 1983). The structure parameters are listed in Table 2.

The determined structure, though apparently rather complex, is actually based on a simple and elegant

* Powder data, anisotropic thermal parameters and structure factors for both compounds and stereoviews of both structures have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38935 (29 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) in CsNa₂Cl₃·2H₂O*

Cs—Cl(2)(×2)	3·4286 (4) Å	O—Cl(1)	3·1496 (19) Å
—Cl(1)(×2)	3·5339 (6)	—Cl(1)	3·2322 (15)
—Cl(1)(×2)	3·6914 (6)	—Cl(1)	3·6081 (15)
—Cl(1)(×2)	3·8313 (7)	—Cl(2)	3·6428 (19)
—O(×2)	3·8204 (18)	—Cl(1)	3·7299 (22)
—O(×2)	3·9568 (20)	—Cl(1)	3·7585 (19)
		—Cl(2)	3·8438 (19)
Na(1)—Cl(1)(×2)	2·8009 (5)	—Cl(2)	3·8464 (19)
—Cl(2)(×2)	2·8802 (4)	—H(1)	0·97 (4)
—O(×2)	2·3932 (17)	—H(2)	0·98 (4)
Na(2)—Cl(1)(×2)	2·8421 (5)		
—Cl(2)	3·0092 (14)		
—Cl(2)	2·8230 (14)		
—O(×2)	2·3584 (19)		

principle. The unit-cell volume is just 12 times larger than the cubic cell of CsCl ($a = 4·121$ Å). The Cl atoms in the monoclinic crystal all lie close to the nodes of the CsCl framework, but $\frac{2}{3}$ of the Cs atoms are replaced by H₂O molecules. Na atoms are then inserted in Cl₄ squares on cubic face centers between pairs of H₂O molecules. Fig. 3 shows a projection of the structure along the b axis. The simple cubic Cl framework is shown as a line network, and the direction of view is along a cubic face diagonal ($\sqrt{2}a_{\text{CsCl}} = 5·827$ Å; $b_{\text{mon}} = 5·831$ Å). The Cs atoms lie in layers normal to the cube diagonal (monoclinic a axis), and the Na atoms and H₂O molecules form coiled chains extended parallel to the c axis.

The Cs atoms, in addition to the eight Cl atoms at the coordination-cube corners, have six next-nearest neighbors: two Cs atoms (as in cubic CsCl), and four H₂O molecules. The Cs—H₂O interatomic distances are shown in Table 3.

Fig. 4 shows an oblique view of a portion of the structure showing how the —H₂O—Na—H₂O—Na chains lie side by side in a layer parallel to the bc plane. The interatomic distances in the structure are listed in Table 3. The distances Na—H₂O (avg. 2·38 Å) and Na—Cl (avg. 2·84 Å; 2·82 Å in NaCl) are perfectly normal, and show a remarkably good fit of these substituents in a CsCl structure that is only slightly distorted. The H₂O molecules are displaced from the

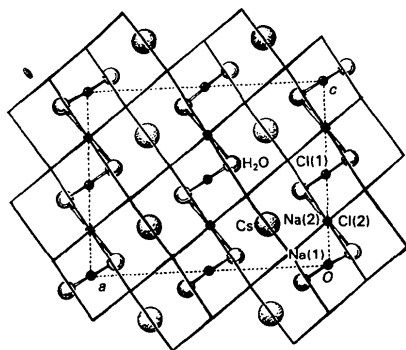


Fig. 3. Projection of the structure of CsNa₂Cl₃·2H₂O along the b axis. Cl atoms are not shown, but they are located at the nodes of the simple cubic lattice indicated by solid lines.

cube centers away from the Na atoms and toward an opposite cube edge. Here they participate with Cl in two Cl—H—O hydrogen bonds of length 3·145 and 3·242 Å, at an angle of 84·2°. All other H₂O—Cl distances are greater than 3·6 Å. These hydrogen bonds must play an important role in stabilizing the structure.

Images of the two H atoms can be discerned at the expected locations in the electron density difference map, appearing as rather sharp peaks reaching a height of 0·6 e Å⁻³. A section containing the O and two Cl(1) positions is shown in Fig. 5, which shows the H maxima. An attempt to refine their positions by least-squares analysis showed an uncertainty of H position of more than 0·05 Å, and atom H(2) converges on a position which is 0·75 Å from O. The coordinates given in Table 2 are taken instead from the peak centers of Fig. 5, which conform well to the expected O—H bond lengths of the H₂O molecule.

Cesium—sodium—chloride cubic solid solution

Zemczuzny & Rambach (1910) found no detectable solid solution in either end member of the anhydrous system NaCl—CsCl. When we compared the unit-cell

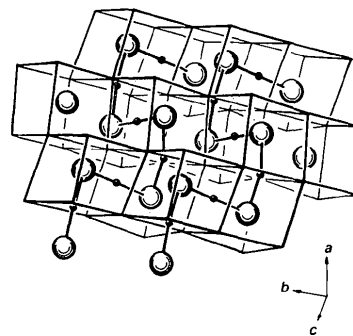


Fig. 4. Oblique view of a portion of the structure of CsNa₂Cl₃·2H₂O showing the arrangement of the (Na—H₂O)_n chains. The Cl framework is shown as in Fig. 3.

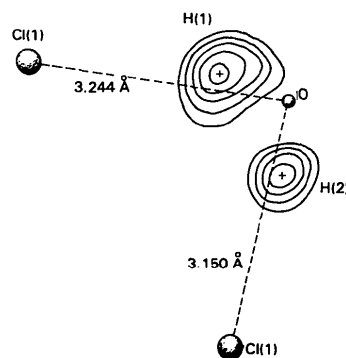


Fig. 5. Difference electron density section in the plane containing H₂O and 2Cl(1) atoms. Contours at 0·2, 0·3, 0·4, 0·5, 0·6 e Å⁻³. (A sharp minimum at the Cl atom is not shown.)

parameters for NaCl and CsCl cooled from a molten mixture containing 75 wt % NaCl only slight changes from established values [for NaCl, Swanson & Fuyat (1953); for CsCl, Pöyhönen & Ruuskanen (1964)] for the pure end members were found:

	NaCl	CsCl
Pure	5.6402 Å	4.1200 Å
Mixed melt	5.6423 (8)	4.1225 (4).

From these data we conclude that NaCl from mixed anhydrous melts does not contain more than 0.2 mol % CsCl in solid solution. The slight increase in the CsCl cell parameter is anomalous, but may be affected by water absorbed by deliquescence in the presence of NaCl.

In the aqueous system with which we are concerned, we found that the cubic cell parameter of CsCl is hardly affected by the introduction of NaCl into the crystal. For a series of cubic crystals that contained as much as 38 mol % NaCl, the cubic unit-cell parameters showed a slight increase but persisted within the range 4.120–4.123 Å (see Fig. 5). As the molar volume of NaCl (44.8 Å³) is much smaller than that of CsCl (69.9 Å³), these solid solutions clearly must also contain H₂O. This possibility was first suggested by the revelation of the crystal structure of CsNa₂Cl₃·2H₂O, which showed how units of NaCl·H₂O can be introduced into the CsCl structure with only slight distortion.

Further information on the character of the solid solutions is provided by index-of-refraction measurements. The values fall regularly as NaCl content increases, but more rapidly than would be expected for anhydrous phases on the basis of molal refractivities (dashed line, Fig. 6). If we use refractivity values derived from the separate components: $k(\text{NaCl})=0.249$, $k(\text{CsCl})=0.161$, and $k(\text{H}_2\text{O})=0.348$ (from average n of the compound), the Gladstone–Dale law, $n-1 = D \sum k_i p_i$ (D = density, p = weight fraction), gives excellent agreement with observed refractive indices, provided H₂O is included in the composition according to $(1-x)(\text{CsCl}) \cdot x(\text{NaCl}) \cdot x(\text{H}_2\text{O})$, or $\text{Cs}_{1-x}(\text{Na} \cdot \text{H}_2\text{O})_x \text{Cl}$ (solid line, Fig. 6). Subsequent analyses of dried samples of the cubic solid solutions did in fact show the presence of H₂O in equimolar amount of NaCl (Chou *et al.*, 1983).

An attempt was made to find direct evidence for the introduction of Na at the site $\frac{1}{2}, \frac{1}{2}, 0$ in the cubic CsCl unit cell by measuring intensities from a crystal containing approximately 15 mol % NaCl. The crystal was ground into a sphere and all intensities measured with Mo $K\alpha$ radiation in one hemisphere in the range $2\theta < 100^\circ$. The independent data set contained 104 reflections. Refinement of thermal and extinction parameters with the assumption of full occupancy by CsCl led directly to $R=0.018$. The

difference map showed a weak maximum at $\frac{1}{2}, \frac{1}{2}, 0$, and an anomalously large depression at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$, the Cs site. All attempts to introduce Na and H₂O into a model for least-squares analysis of occupancy and thermal parameters failed because it was impossible to avoid many cross correlations greater than 0.85. Unfortunately, direct evidence for the presence of Na is marginal.

Nevertheless, we can now understand the structural basis for the solid solution $\text{Cs}_{1-x}(\text{Na} \cdot \text{H}_2\text{O})_x \text{Cl}$ in terms of the structural properties of the new compound. H₂O, rather than Na (which is far too small), replaces Cs at the center of the Cl₈ cube, and at the same time Na atoms are inserted in the cube-face centers between pairs of H₂O molecules. The Na atoms thus are octahedrally coordinated, forming NaCl₄(H₂O)₂ groups. In this grouping, each Na must be associated with two H₂O molecules, as Na at a cube-face center cannot be in contact with Cs at a body center. Thus, in order to maintain charge balance, randomly coiled chains of the type $-\text{Na}-\text{H}_2\text{O}-\text{Na}-\text{H}_2\text{O}-$ must be formed, which may be terminated by Cs vacancies, or be looped into rings. As the H₂O molecule is strongly displaced toward one cube edge, both to form O–H–Cl hydrogen bonds and to allow room for Na–O contact, H₂O can only associate with two Na atoms at right angles and not in a straight line. This restriction accounts for the coiled arrangement of the chains in the compound CsNa₂Cl₃·2H₂O. A fragment of the solid-solution structure consisting of 18 cubic cells is depicted in Fig. 7.

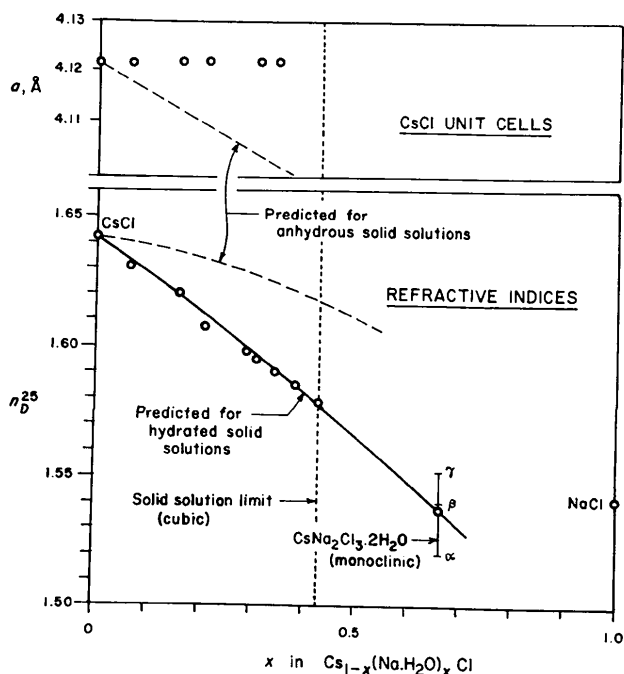


Fig. 6. Unit-cell parameters and refractive indices of CsCl-NaCl·H₂O solid-solution phases.

Dicesium calcium tetrachloride dihydrate

After the principles of the cesium–sodium–chloride–water structures became understood, it occurred to us that calcium might play a role similar to sodium in analogous structures. The system $\text{CsCl}-\text{CaCl}_2-\text{H}_2\text{O}$ has also been studied by Plyushchev, Tulinova, Kutznetsova, Korovin & Shipetina (1957), and the ternary diagram representing their results is shown in Fig. 8. Three compounds were found, all previously known: CsCaCl_3 , Cs_5CaCl_7 , and $\text{Cs}_2\text{CaCl}_4 \cdot 2\text{H}_2\text{O}$. The hydrate, which is the one of interest to us, was first prepared and described by Jamieson (1917). No solid-solution phases appeared in the study by Plyushchev *et al.*

We prepared $\text{Cs}_2\text{CaCl}_4 \cdot 2\text{H}_2\text{O}$ as large, prismatic, triclinic crystals from solutions containing stoichiometric concentrations of the components. They are triclinic, and their crystallographic data are given in the *Abstract*. The crystals commonly form contact twins on $(\bar{1}01)$, which corresponds to a pseudocube face in the CsCl sublattice. This face also

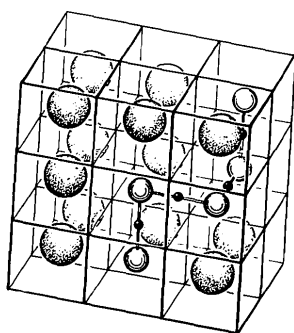


Fig. 7. Oblique view of 18 CsCl unit cells showing probable random arrangement of $(\text{Na}-\text{H}_2\text{O})_n$ chains in the cubic solid-solution structure.

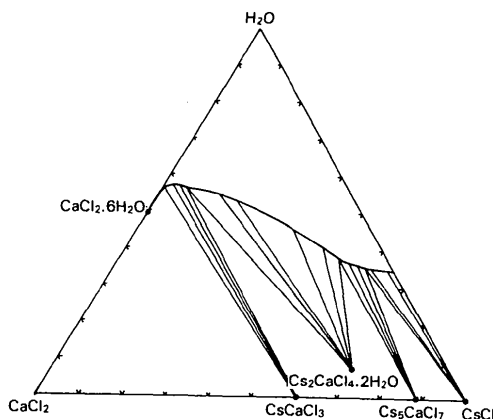


Fig. 8. The system $\text{CsCl}-\text{CaCl}_2-\text{H}_2\text{O}$ as determined by Plyushchev, Tulinova, Kutznetsova, Korovin & Shipetina (1957). Graduations are in wt %.

Table 4. *Experimental details for $\text{Cs}_2\text{CaCl}_4 \cdot 2\text{H}_2\text{O}$*

Crystal size:	0.18 × 0.29 × 0.72 mm		
Corrections:	Lorentz, polarization, absorption, dispersion, isotropic extinction		
Reflections measured:	1613 independent, with $2\theta < 60^\circ$ ($\text{Mo K}\alpha$ radiation)		
Reflections used for refinement:	1477 with $I > 2\sigma(I)$; weights $w = 1/\sigma^2$ (from counting statistics)		
Refinement:	44 variables; to $R = 0.079$, $R_w = 0.110$		
$(\Delta/\sigma)_{\text{max}}$	= 0.25		

Table 5. *Structure parameters and root-mean-square thermal motions of atoms in $\text{Cs}_2\text{CaCl}_4 \cdot 2\text{H}_2\text{O}$*

$$\bar{u}^2 = \frac{1}{3} \sum_i U_{ii}$$

	x	y	z	\bar{u} (Å)
Cs	0.1568 (1)	0.1207 (1)	0.2557 (1)	0.128 (3)
Ca	0.5	0.5	0.5	0.08 (2)
Cl(1)	0.6294 (4)	0.1697 (4)	0.2357 (5)	0.11 (1)
Cl(2)	0.1060 (4)	0.6324 (5)	0.2638 (5)	0.12 (1)
O	0.3789 (16)	0.3443 (15)	0.7582 (15)	0.16 (4)

shows perfect cleavage. X-ray powder data,* were used to refine the unit-cell parameters [for 56 reflections, $\sigma(2\theta) = 0.016^\circ$]. The intensity data showed pronounced acentric statistical distributions, so initially the space group was assumed to be $P1$. The Cs atom positions were obtained from a Patterson ($E^2 - 1$) map, and the structure built up with the aid of successive electron density maps. As atoms were added to the structure, it soon became apparent that the true symmetry is $P\bar{1}$. The statistics were likely distorted by a large extinction effect, which suppressed strong reflections, especially at low Bragg angles. The structure refined smoothly in $P\bar{1}$. The final structure parameters are listed in Table 5. A projection of the structure along the c axis is shown in Fig. 9.

Our expectation about the structure of this compound is fully confirmed: it consists of a cubic CsCl framework in which half the Cs atoms are replaced by H_2O molecules, and Ca atoms are inserted in cubic

* See deposition footnote.

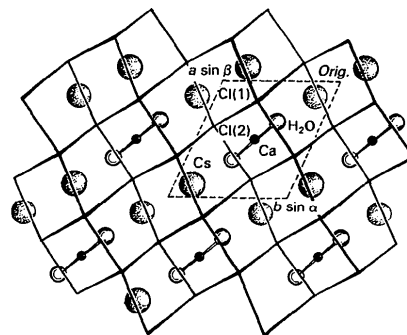


Fig. 9. Projection of the structure of $\text{Cs}_2\text{CaCl}_4 \cdot 2\text{H}_2\text{O}$ along the c axis. The Cl framework is depicted as in Fig. 3.

Table 6. *Interatomic distances (Å) in Cs₂CaCl₄·2H₂O*

Cs-Cl(1)	3.447 (3) Å	O-Cl(1)	3.153 (9) Å
-Cl(1)	3.492 (3)	-Cl(2)	3.267 (12)
-Cl(2)	3.536 (3)	-Cl(2)	3.549 (9)
-Cl(2)	3.545 (3)	-Cl(1)	3.613 (10)
-Cl(1)	3.571 (3)	-Cl(1)	3.626 (13)
-Cl(1)	3.604 (3)	-Cl(2)	3.649 (13)
-Cl(2)	3.710 (4)	-Cl(2)	3.786 (9)
-Cl(1)	3.831 (4)	-Cl(1)	3.888 (13)
-O	3.624 (9)		
-O	3.833 (11)	Ca-Cl(2)(×2)	2.711 (3)
-O	4.151 (12)	-Cl(1)(×2)	2.739 (3)
-O	4.165 (9)	-O(×2)	2.367 (12)

	Cs ₂ CaCl ₄ ·2H ₂ O	Cs ₂ MnCl ₄ ·2H ₂ O	Rb ₂ MnCl ₄ ·2H ₂ O
<i>a</i> (Å)	6.904	6.66	6.48
<i>b</i> (Å)	7.513	7.27	7.01
<i>c</i> (Å)	5.877	5.74	5.66
α (°)	92.28	92.2	92.3
β (°)	96.13	95.7	95.2
γ (°)	65.23	67.0	66.7
<i>V</i> (Å ³)	275.2	254.6	232.3

References

- CHOU, I.-M. & LEE, R. D. (1983). *J. Chem. Eng. Data*, **28**, 390-393.
 CHOU, I.-M. & ROMANKIW, L. A. (1983). *J. Chem. Eng. Data*, **28**, 396-398.
 CHOU, I.-M., ROMANKIW, L. A., EVANS, H. T. JR & KONNERT, J. A. (1982). *Trans. Geophys. Union*, **63**, 465.
 CHOU, I.-M., ROMANKIW, L. A., EVANS, H. T. JR & KONNERT, J. A. (1983). *J. Chem. Eng. Data*, **28**, 393-396.
 CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321-324.
 EVANS, H. T. JR, KONNERT, L. A., CHOU, I.-M. & ROMANKIW, L. A. (1982). *Am. Crystallogr. Assoc. Progr. Abstr.* **10**, 32.
 JAMIESON, G. S. (1917). *Am. J. Sci.* **43**, 67-68.
 JENSEN, S. J. (1964). *Acta Chem. Scand.* **18**, 2085-2097.
 PLYUSHCHEV, V. E., TULINOVA, V. B., KUTZNETSOVA, G. P., KOROVIN, S. S. & PETROVA, R. G. (1957). *Zh. Neorg. Khim.* **2**, 2212-2220; Engl. trans. *J. Inorg. Chem. USSR*, **2**, 357-368.
 PLYUSHCHEV, V. E., TULINOVA, V. B., KUTZNETSOVA, G. P., KOROVIN, S. S. & SHIPETINA, N. S. (1957). *Zh. Neorg. Khim.* **2**, 2654-2660; Engl. trans. *J. Inorg. Chem. USSR*, **2**, 267-275.
 PÖYHÖNEN, J. & RUUSKANEN, A. (1964). *Ann. Acad. Sci. Fenn. Ser. A*, **6**, No. 146, 1-12.
 STEWART, J. M. (1976). Editor, XRAY76. Tech. Rep. TR-446, Computer Science Center, Univ. of Maryland, College Park, Maryland.
 SWANSON, H. E. & FUYAT, R. K. (1953). *Natl. Bur. Stand. US Circ.* **539**, Vol. II, 41-43.
 ZEMCZUZYNY, S. & RAMBACH, F. (1910). *Z. anorg. Chem.* **65**, 403-428.

face centers between pairs of H₂O molecules. Ca atoms are coordinated octahedrally as CaCl₄(H₂O)₂. Chain formation is not required for charge balance in this structure, and the H₂O-Ca-H₂O groups are isolated from each other. The cubic chlorine framework is only a little more distorted than in the Na compound. Hydrogen bonds are formed between H₂O molecules and the pair of Cl atoms at one cube edge opposite the Ca atom, as in the Na compound. Table 6 lists the bond lengths in the structure.

A subsequent search for other double-salt hydrates containing CsCl that might follow a structural principle similar to that found in this work led to two other compounds: Cs₂MnCl₄·2H₂O and Rb₂MnCl₄·2H₂O. The structures of these crystals have been reported by Jensen (1964). They are, in fact, isostructural with Cs₂CaCl₄·2H₂O. After transforming Jensen's unit cells by (00 $\bar{1}$ /100/0 $\bar{1}$ 0), they may be compared with that given in the *Abstract* as follows:

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Electron Density Distribution in an Ilmenite-Type Crystal of Cobalt(II) Titanium(IV) Trioxide

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Abstract

The electron density distribution in a crystal of CoTiO₃ has been investigated with the single-crystal X-ray diffraction method. Deformation densities were observed around the Co²⁺ ion, which is qualitatively explained with the high-spin electron configuration

of a *d*⁷ ion in an octahedral field. The Ti⁴⁺ ion lies in a negative region of the deformation density map, and a positive peak exists on the threefold axis at a position 0.63 Å from the Ti⁴⁺ ion towards the Co²⁺ ion. It is proposed that these negative and positive peaks are caused by deformation of the electron cloud to shield the positive charge of the neighbouring Co²⁺