Crystallographic investigations of [Mg(H₂O)₆]XCl₃ double salts (X⁺ = K⁺, Rb⁺, Cs⁺, NH₄⁺): Crystal structure of [Mg(H₂O)₆]CsCl₃

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Abstract

The crystal structure of the double salt complex $MgCl_2 \cdot CsCl \cdot 6H_2O$ has been determined by single-crystal X-ray diffraction methods. The phase is triclinic, space group $P1$, with unit-cell dimensions $a = 6.7507(7)$, $b = 13.495(2)$, $c = 6.750(1)$ Å, $\alpha = 90.13(1)$, $\beta = 91.15(1)$, $\gamma = 90.18(1)°$. The crystal structure consists of a network of corner-sharing $[CsCl_6]$ octahedra and isolated $[Mg(H_2O)_6]^{2+}$ octahedra that occupy holes in the $[CsCl_6]$ network. The atomic arrangement can be considered as a perovskite-type structure in which the large A cation of the perovskite-type ABC_3 structure is replaced by the $[Mg(H_2O)_6]^{2+}$ complex. The structure is similar to that of $[Mg(H_2O)_6]RbCl_3$ and $[Mg(H_2O)_6]NH_4Cl_3$, although it differs from that of $[Mg(H_2O)_6]KCl_3$ (carnallite), which has a hexagonal $BaTiO_3$-type structure. To explain the existence of two structure types in $[Mg(H_2O)_6]XCl_3$ ($X^+ = K^+, Rb^+, Cs^+, NH_4^+$) compounds, a tolerance factor, t, is calculated using an ionic radius of 2.90 Å for $[Mg(H_2O)_6]^{2+}$ (estimated in this work). The calculated t values are 1.04, 1.00, 0.95, and 0.97 for the K^+, Rb^+, Cs^+, and NH_4^+ ions, respectively. The t value of the K^+ compound exceeds the stable region $0.80 \leq t \leq 1.00$ of the perovskite-type structure.

Introduction

Alkali metal ions are often found to be concentrated in sea water or nonmarine brines in the course of evaporation. It is well known that K^+ ions accumulate as carnallite {$[Mg(H_2O)_6]KCl_3$} at the late stage of evaporation (e.g., Harvie et al., 1980; Lowenstein et al., 1989). The structure of carnallite is constructed from a network of face-sharing $[KCl_6]$ octahedra with isolated $[Mg(H_2O)_6]^{2+}$ octahedra occupying the holes in the $[KCl_6]$ network (Schlemper et al., 1985). The atomic arrangement corresponds to the hexagonal $BaTiO_3$-type structure of ABC_3 compounds (Burbank and Evans, 1948).

The structures of $[Mg(H_2O)_6]RbCl_3$ (Waizumi et al., 1991) and $[Mg(H_2O)_6]NH_4Cl_3$ (Nakayasu et al., 1983), compounds that are chemically similar to carnallite, have been determined. The structure of these compounds consists of a network of corner-sharing $[RbCl_6]$ or $[(NH_4)Cl_6]$ octahedra and isolated $[Mg(H_2O)_6]^{2+}$ octahedra that are situated in holes in the $[RbCl_6]$ or $[(NH_4)Cl_6]$ networks. The structure is thus analogous to that of perovskite (Wells, 1984).

It is of interest that the structure of carnallite is different from that of other compounds with similar composition. In this work we have determined the crystal structure of $[Mg(H_2O)_6]CsCl_3$ in order to assist in the determination of those factors that separate carnallite, $[Mg(H_2O)_6]KCl_3$, from other alkali chloride–magnesium chloride double salts.

Experimental

The $[Mg(H_2O)_6]CsCl_3$ was prepared from a solution of a ternary $MgCl_2$-$CsCl$-H_2O mixture by slow evaporation. The colorless crystal was sealed in a thin-walled glass tube and cooled to 235 K to avoid decomposition. Diffraction intensities were measured using an Enraf-Nonius CAD-4 automated four-circle diffractometer with graphite-monochromated $MoK\alpha$ radiation ($\lambda = 0.71073$ Å). The unit-cell parameters were determined from the setting angles ($22.56° \leq 2\theta \leq 28.06°$) of 25 reflections. The experimental data for the crystal structure analysis are tabulated in Table 1. All the reflections were corrected for Lorentz and polarization effects. An empirical absorption correction using DIFABS (Walker and Stuart, 1983) was applied after isotropic refinement, with corrections in the range 0.82–1.20. The corrected intensities did not unambiguously show whether the crystal has the triclinic space group $P1$ or $P\bar{1}$. The intensity-statistics

TABLE 1. Crystal and structure refinement data

Formula	CsMgCl₃O₆H₁₂
Molecular weight	371.66
Crystal system	triclinic
Space group	P1
a (Å)	6.7507(7)
b (Å)	13.495(2)
c (Å)	6.750(1)
α (°)	90.13(1)
β (°)	91.15(1)
γ (°)	90.18(1)
V (Å³)	614.7(2)
Z	2
$F(000)$	356
D_{calc} (g/cm³)	2.008
λ (Å)	0.71073
μ (cm⁻¹)	48.3
Crystal dimensions (mm)	0.3 × 0.3 × 0.4
2θ range	1° < 2θ < 60°
Scan width (°)	0.70 + 0.35 tanθ
Scan type	ω − 2θ
Scan rate (°min⁻¹) in ω	4
Standard reflections	3
Time between standards (min)	120
Range of h, k, l	−9 ≤ h ≤ 9, −18 ≤ k ≤ 18, 0 ≤ l ≤ 9
Total data collected	3888
Unique data with $|I_o| > 3.0\sigma\,(I_o)$	3399
Parameters refined	293
R; R_w	0.036, 0.051
S	1.23

TABLE 3. Positional coordinates and isotropic thermal parameters for H atoms

Atom	x	y	z	B_{iso} (Å²)
H1A	0.69(2)	0.266(8)	0.15(2)	3.0
H1B	0.59(2)	0.359(8)	0.19(2)	3.2
H2A	0.53(2)	0.408(8)	0.71(2)	3.0
H2B	0.72(2)	0.404(8)	0.59(2)	3.3
H3A	0.19(2)	0.366(8)	0.45(2)	2.9
H3B	0.16(1)	0.280(8)	0.30(2)	2.5
H4A	0.83(2)	0.126(8)	0.55(2)	2.6
H4B	0.80(2)	0.210(9)	0.70(2)	3.8
H5A	0.30(1)	0.082(7)	0.47(1)	2.2
H5B	0.43(2)	0.098(8)	0.25(2)	3.2
H6A	0.41(1)	0.146(8)	0.82(2)	2.5
H6B	0.28(2)	0.243(9)	0.83(2)	3.8
H7A	0.32(1)	0.785(7)	0.16(1)	2.0
H7B	0.45(2)	0.862(8)	0.17(2)	3.9
H8A	0.28(2)	0.595(8)	0.47(2)	3.0
H8B	0.46(2)	0.583(8)	0.30(2)	3.3
H9A	0.71(2)	0.924(8)	0.52(2)	3.1
H9B	0.57(2)	0.925(8)	0.69(2)	2.8
H10A	0.56(2)	0.630(8)	0.79(2)	2.8
H10B	0.69(1)	0.720(7)	0.84(2)	2.2
H11A	0.82(2)	0.746(9)	0.28(2)	4.2
H11B	0.81(2)	0.66(1)	0.42(2)	5.1
H12A	0.18(2)	0.843(8)	0.54(2)	2.8
H12B	0.18(2)	0.773(8)	0.70(2)	2.9

Note: Numbers in parentheses are estimated standard deviations.

calculated, however, indicated that the noncentrosymmetric space group P1 was acceptable.

The heavy atom method was applied and the structure was refined by the full matrix least-squares method. All calculations were performed on a Micro VAX II computer using the Enraf-Nonius SDP set of computer programs (Frenz, 1985). Several cycles of refinement (on F) for atomic positions, including anisotropic thermal pa-

TABLE 2. Positional coordinates and equivalent isotropic temperature factors for non-H atoms

Atom	x	y	z	B_{eq} (Å²)
Cs1	0	0	0	2.3
Cs2	0.01495(8)	0.50000(4)	−0.01483(8)	2.4
Mg1	0.5042(8)	0.2484(5)	0.492(1)	1.5
Mg2	0.5025(7)	0.7483(4)	0.4891(8)	1.4
Cl1	0.0225(3)	−0.0026(2)	0.4965(3)	2.2
Cl2	−0.0096(3)	0.5054(1)	0.4878(3)	2.2
Cl3	0.5004(3)	0.0040(1)	−0.0224(3)	2.2
Cl4	0.5090(3)	0.4960(2)	0.0098(3)	2.4
Cl5	0.0061(7)	0.2491(4)	0.9951(9)	2.5
Cl6	0.0066(7)	0.7494(4)	0.9896(8)	2.4
O1	0.6014(8)	0.2909(5)	0.2168(9)	2.4
O2	0.580(1)	0.3883(6)	0.597(1)	3.7
O3	0.2234(9)	0.3007(5)	0.418(1)	2.6
O4	0.7744(8)	0.1924(4)	0.5844(9)	2.2
O5	0.4185(8)	0.1139(4)	0.3833(9)	2.0
O6	0.3960(9)	0.2127(5)	0.7628(9)	2.6
O7	0.4087(9)	0.8072(5)	0.2174(9)	2.6
O8	0.4022(9)	0.6158(4)	0.411(1)	2.9
O9	0.619(1)	0.8902(4)	0.576(1)	2.5
O10	0.5794(8)	0.6981(5)	0.7684(9)	2.2
O11	0.7738(9)	0.7160(5)	0.383(1)	2.6
O12	0.2290(8)	0.7941(5)	0.5916(9)	2.4

Note: Numbers in parentheses are estimated standard deviations.

rameters of ions, were carried out with the weighting scheme $w = \{[\sigma(|F_o|)]^2 + (0.020|F_o|)^2 + 1\}^{-1}$. Electron density associated with H atoms could be discerned at the expected locations in the difference map, and H atoms were refined isotropically. Difference-Fourier maps calculated using the final parameters showed maximum and minimum electron-density peaks of 0.7 and −2.7 e Å⁻³, located around the Cs⁺ ions.

The final positional parameters are listed in Tables 2 and 3 for non-H and H atoms, respectively. Table 4[1] records anisotropic thermal parameters for non-H atoms. Selected interatomic distances and angles are given in Table 5, and the distances between the Mg²⁺ and Cl⁻ ions are given in Table 6. H-bond distances and angles are shown in Table 7. Observed and calculated structure factors are listed in Table 8.

RESULTS

The crystal structure of [Mg(H₂O)₆]CsCl₃ is shown in Figure 1. The atomic arrangement consists of a network of corner-sharing [CsCl₆] octahedra with isolated [Mg(H₂O)₆]²⁺ octahedra that occupy the holes in the [CsCl₆] network (Fig. 2). The structure is isostructural with that of [Mg(H₂O)₆]RbCl₃ and [Mg(H₂O)₆]NH₄Cl₃. Cs⁺ ions are octahedrally coordinated by six Cl⁻ ions. Each Cl⁻ ion is surrounded by two Cs⁺ ions and four H₂O molecules, each of which is associated with one [Mg(H₂O)₆]²⁺ ion.

[1] Copies of Tables 4, 6, 7, and 8 may be ordered as Document AM-91-475 from the Business Office, Mineralogical Society of America, 1130 Seventeenth Street NW, Suite 330, Washington, DC 20036, U.S.A. Please remit $5.00 in advance for the microfiche.

TABLE 5. Interatomic distances (Å) and angles (°)

Cs1–Cl1*	3.405(2)	Cs2–Cl2	3.401(2)
–Cl3**	3.374(2)	–Cl4	3.337(2)
–Cl5*	3.361(6)	–Cl6*	3.366(6)
–Cl1	3.352(2)	–Cl2*	3.359(2)
–Cl3	3.385(2)	–Cl4**	3.424(2)
–Cl6†	3.383(6)	–Cl5*	3.387(6)
Mg1–O1†	2.062(9)		
–O3	2.076(8)		
–O5	2.035(8)		
–O2	2.08(1)		
–O4	2.062(8)		
–O6	2.041(9)		
O1–Mg1–O2	88.5(4)	O1–Mg1–O3	89.6(3)
–O4	94.6(3)	–O5	91.0(4)
–O6	176.7(4)	O2–Mg1–O3	89.4(4)
O2–Mg1–O4	91.1(4)	–O5	177.5(4)
–O6	90.0(4)	O3–Mg1–O4	175.7(4)
O3–Mg1–O5	88.1(3)	–O6	87.4(3)
O4–Mg1–O5	91.4(3)	O4–Mg1–O6	88.3(3)
O5–Mg1–O6	90.4(3)		
Mg2–O7	2.088(8)		
–O9	2.144(8)		
–O11	2.028(8)		
–O8	1.977(8)		
–O10	2.061(8)		
–O12	2.080(8)		
O7–Mg2–O8	90.8(3)	O7–Mg2–O9	90.1(3)
–O10	175.3(4)	–O11	91.9(3)
–O12	85.5(3)	O8–Mg2–O9	178.5(4)
O8–Mg2–O10	91.5(3)	–O11	91.0(3)
–O12	93.3(3)	O9–Mg2–O10	87.7(3)
O9–Mg2–O11	87.8(3)	–O12	88.0(3)
O10–Mg2–O11	92.2(3)	O10–Mg2–O12	90.2(3)
O11–Mg2–O12	175.1(4)		

Note: Estimated standard deviations are in parentheses.
   * Unit-cell translation: 0, 0, −1.
  ** Unit-cell translation: −1, 0, 0.
   † Unit-cell translation: 0, −1, −1.
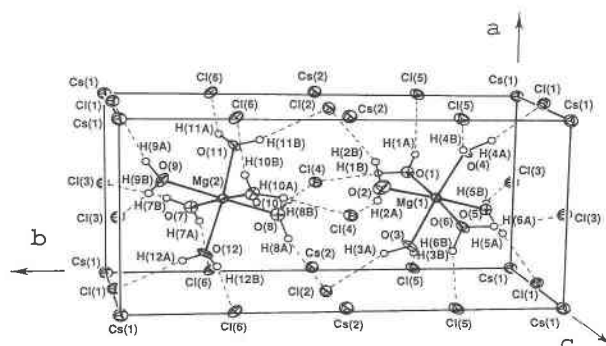

Fig. 1. An ORTEP (Johnson, 1965) drawing of the structure of [Mg(H₂O)₆]CsCl₃ with thermal ellipsoids scaled at the 30% probability level. H bonds are represented by dashed lines.

The Mg-O bond lengths in the two independent [Mg(H₂O)₆]²⁺ groups lie in the range 2.035(8) to 2.08(1) Å for Mg1 and 1.977(8) to 2.144(8) Å for Mg2 (Table 5). The average Mg-O bond distance of 2.061 Å is slightly longer than those of [Mg(H₂O)₆]KCl₃ (2.045 Å, Schlemper et al., 1985), [Mg(H₂O)₆]RbCl₃ (2.046 Å, Waizumi et al., 1991), and [Mg(H₂O)₆]NH₄Cl₃ (2.058 Å, Nakayasu et al., 1983). The distance between a Cl⁻ ion and an O atom varies from 3.130(8) to 3.293(7) Å. The average distance, 3.204 Å, is also slightly longer than the average distance of Cl···O H bonds in [Mg(H₂O)₆]KCl₃ (3.169 Å, Schlemper et al., 1985), [Mg(H₂O)₆]RbCl₃ (3.166 Å, Waizumi et al., 1991), and [Mg(H₂O)₆]NH₄Cl₃ (3.17 Å, Nakayasu et al., 1983).

DISCUSSION

The average X^+-Cl⁻ distances for the series of compounds [Mg(H₂O)₆]XCl₃ (X^+ = K⁺, Rb⁺, Cs⁺, NH₄⁺) are compared with the sum of the ionic radii of X^+ (including Na⁺) and Cl⁻ in Table 9. The distance between Cs⁺ and Cl⁻ ions in [Mg(H₂O)₆]CsCl₃ ranges from 3.337 to 3.424 Å. The average distance of 3.378 Å is significantly shorter than the sum of their ionic radii, 3.48 Å. The average of the Rb⁺-Cl⁻ bond lengths in [Mg(H₂O)₆]RbCl₃ is close to the sum of the ionic radii of Rb⁺ and Cl⁻. The average

NH₄⁺-Cl⁻ distance in [Mg(H₂O)₆]NH₄Cl₃ is smaller than the sum of the ionic radii of NH₄⁺ and Cl⁻. Conversely, the average K⁺-Cl⁻ distance in [Mg(H₂O)₆]KCl₃ is longer than the sum of the ionic radii of K⁺ and Cl⁻ ions.

For X^+ = Rb⁺, Cs⁺, and NH₄⁺, [Mg(H₂O)₆]XCl₃ has the perovskite-type structure with [XCl₆] octahedra linked by sharing corners between adjacent octahedra. Conversely, for X^+ = K⁺ it has the hexagonal BaTiO₃-type structure in which two-thirds of the [KCl₆] octahedra share faces.

For the ideal perovskite structure of ABC₃ compounds (cubic), the following relationship exists among the radii of the A, B, and C ions:

$$\sqrt{2}(r_A + r_C) = 2(r_B + r_C) \qquad (1)$$

where the radius of the A cation corresponds to eightfold coordination, and the radii of the B cation and the C anion are those of sixfold coordinated ions. The relationship shows that the ionic size of the B cation is strongly influenced by the A cation in the ideal perovskite structure. A degree of variation in the ionic radius of the B cation is permitted in compounds with the perovskite structure. This variation in ionic size can be explained in terms of a tolerance factor as defined by Goldschmidt (1926):

$$t = \frac{r_A + r_C}{\sqrt{2}(r_B + r_C)} \qquad (2)$$

The formation of the perovskite structure occurs for tolerance factors between 0.80 and 1.00 (Wells, 1984).
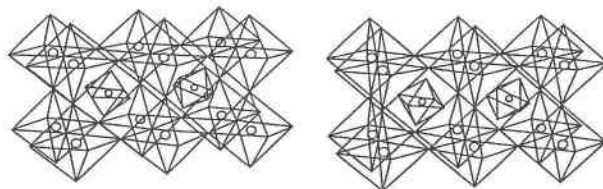

Fig. 2. Stereoscopic drawing of the [Mg(H₂O)₆]CsCl₃ crystal structure. Large and small octahedra are [CsCl₆] and [Mg(H₂O)₆]²⁺, respectively.

TABLE 9. Distances between X^+ and Cl$^-$ ions and the sum of the ionic radii (Å)

| X^+ cation | Interatomic distance in double salt ([Mg(H₂O)₆]XCl₃) | | Sum of ionic radii (Cl$^-$ = 1.81 Å)* | Tolerance factor** | |
	Average	Reference		(A)	(B)
Na$^+$	—	—	2.83 (Na$^+$ = 1.02)*	1.34	1.18
K$^+$	3.238	Schlemper et al. (1985)	3.19 (K$^+$ = 1.38)*	1.19	1.04
Rb$^+$	3.327	Waizumi et al. (1991)	3.33 (Rb$^+$ = 1.52)*	1.14	1.00
Cs$^+$	3.378	this work	3.48 (Cs$^+$ = 1.67)*	1.09	0.95
NH₄$^+$	3.33	Nakayasu et al. (1983)	3.42 (NH₄$^+$ = 1.61)†	1.11	0.97
			3.29 (NH₄$^+$ = 1.48)‡	1.15	1.01

Note: The ionic radii refer to the ions in sixfold coordination.
* Shannon (1976).
** Calculated using the assumption that the ionic radius of [Mg(H₂O)₆]$^{2+}$ is (A) 3.54 Å and (B) 2.90 Å.
† Khan and Baur (1972).
‡ Pauling (1960).

For t values smaller than 0.8, the ilmenite (FeTiO₃) structure is formed (Wells, 1984). Application of the tolerance factor may be extended to the formation of the double salt [Mg(H₂O)₆]CsCl₃, in which [Mg(H₂O)₆]$^{2+}$ can be regarded as the A cation in the general formula ABC₃.

The ionic radius of [Mg(H₂O)₆]$^{2+}$ may be estimated from the ionic radius of Mg^{2+} (0.72 Å, Shannon, 1976) and the diameter of an H₂O molecule (2.82 Å, Ben-Naim, 1974) by assuming a spherical structure for the octa-hydrated Mg^{2+} ion, i.e., 0.72 + 2.82 = 3.54 Å. To check the validity of the ionic radius, the t values for the [Mg(H₂O)₆]XCl_3 compounds were calculated using Equation 2, and the results are listed in Table 9. All the values are far beyond the stable range estimated by Wells (1984), even though [Mg(H₂O)₆]RbCl₃, [Mg(H₂O)₆]CsCl₃ and [Mg(H₂O)₆]-NH₄Cl₃ have been shown to have the perovskite-type structure. The obvious conclusion is that the spherical model for the [Mg(H₂O)₆]$^{2+}$ ion is too simple to explain the stability of the perovskite-type compounds.

Because the Rb-Cl distance in [Mg(H₂O)]RbCl₃ is very close to the sum of the individual ionic radii and because in other double salts with similar composition the distance between the alkali metal ion and chloride ion is significantly different from the sum of the radii of the individual ions, [Mg(H₂O)₆]RbCl₃ may be considered to have the most stable structure among them. It is therefore assumed that [Mg(H₂O)₆]RbCl₃ forms a nearly ideal perovskite structure, and we thus normalize to $t = 1$ for [Mg(H₂O)₆]RbCl₃. The resulting value for the radius of the [Mg(H₂O)₆]$^{2+}$ ion is 2.90 Å, which is much smaller than the value 3.54 Å previously calculated. This result suggests that the chloride ion penetrates the assumed spherical hydration sphere of the Mg^{2+} ion on formation of the perovskite structure. Indeed, the Mg-Cl distances determined in the present investigation are 4.653(6)–4.912(6) Å (Table 6), much shorter than the sum of the ionic radii of Cl$^-$ and the simple spherical [Mg(H₂O)₆]$^{2+}$ complex.

According to the structure analysis, the Mg-O-Cl bond bends as a consequence of the formation of an O-H···Cl H bond, and consequently the Cl$^-$ ion can approach the Mg^{2+} ion through the cavity between H₂O molecules in the hydration sphere. Such an atomic arrangement by the H bonding interactions between the H₂O molecule and chloride ion causes the perovskite structure of the [Mg(H₂O)₆]XCl_3 salts to be stable.

If we assume the ionic radius of [Mg(H₂O)₆]$^{2+}$ to be 2.90 Å, then the t values for [Mg(H₂O)₆]CsCl₃ and [Mg-(H₂O)₆]NH₄Cl₃ can be calculated to be 0.95 and 0.97–1.01, respectively (Table 9). Clearly the ionic radius of [Mg(H₂O)₆]$^{2+}$ of 2.90 Å seems more realistic than 3.54 Å. The t value of [Mg(H₂O)₆]KCl₃, which forms the hexagonal BaTiO₃-type structure, becomes 1.04; this value is larger than the upper limit of the accepted range for the formation of a perovskite-type structure.

The CsXF_3 compounds (X^{2+} = Mg^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, and Zn^{2+}) have the hexagonal BaTiO₃ type of structure (Longo and Kafalas, 1969), and the t values of these compounds are 1.06(Mg^{2+}), 1.01(Mn^{2+}), 1.03(Fe^{2+}), 1.05(Co^{2+}), 1.07(Ni^{2+}), and 1.05(Zn^{2+}). The ABC₃ compounds with t larger than 1.00 thus adopt the hexagonal BaTiO₃ structure. The structure of carnallite, different from that of the other [Mg(H₂O)₆]XCl_3-type compounds, may thus be caused by the large t factor.

No ABC₃ compound has been obtained from MgCl₂-NaCl-H₂O solutions (Keitel, 1923). The t value for [Mg(H₂O)₆]NaCl₃ is calculated as 1.18. In this case, the ionic radius of Na$^+$ is too small with respect to the large [Mg(H₂O)₆]$^{2+}$ ion to enable the perovskite structure to form.

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