Refinement of the structure of carnallite, $Mg(H_2O)_6KCl_3$

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Abstract

The unit cell and the atomic parameters of carnallite were refined from three-dimensional X-ray diffraction data ($a = 1.6119(3)$ nm, $b = 2.2472(4)$ nm, $c = 0.9551(2)$ nm, space group: *Pnna*, $Z = 12$). The structural model proposed by Fischer (1973) is confirmed and extended by determining the hydrogen positions and refining anisotropic temperature coefficients. The unique crystal structure of carnallite consists of a network of face-sharing KCl_6 octahedra and of isolated $Mg(H_2O)_6$ octahedra occupying the openings in the KCl network. The water molecules act as charge transmitters between Mg^{2+} and Cl^{1-} ions. The average interatomic distances are 0.2045 and 0.3238 nm, for $Mg–(H_2O)$ and K–Cl, respectively.

Introduction

Leonhardt (1930) determined the unit cell dimensions and the space group of carnallite (Table 1). Andress and Saff (1939) confirmed Leonard's unit cell data but obtained a different space group (Table 1). In the same paper, Andress and Saffe (1939) also reported on the investigation of the unit cell, space group and structure of brom-carnallite: $KMg(H_2O)_6(ClBr)_3$, $a = 1.351$ and $c = 0.677$ nm, space group *P4/n*. They found that magnesium in the structure of brom-carnallite is octahedrally coordinated to water molecules which transmit the magnesium's charge to chlorine or bromine. Potassium is octahedrally coordinated to the anions. They also speculated that the structure of pure carnallite may be an orthorhombic-pseudohexagonal variation of the brom-carnallite structure.

Fischer (1973) prepared a synthetic crystal of carnallite by slow crystallization at 25°C, from a solution containing 1.5 mole% KCl and 98.5 mole% $MgCl_2 \cdot 6H_2O$. He determined the lattice parameters and the space group of this crystal (Table 1). The density calculated from these unit cell parameters, 1.587 g/cm³, compares well with that observed, 1.602 g/cm³.

Using 2001 intensities collected by an equiinclination Weissenberg camera and multiple film method, he deter-

mined the carnallite structure. The correspondence between the observed and calculated structure factors gave a reliability factor (*R*) of 12.2%.

For the initial model, he constructed a complex close-packed structure composed of an *N*-net (of Hermann's 1962 scheme, also known as Kagomé net) of chlorines which is complemented by the magnesium-water octahedra to form a distorted hexagonal close-packed layer. The layers are stacked in a hexagonal close-packed sequence, with potassium occupying the large octahedral voids. He compared the carnallite structure with the tetragonal brom-carnallite structure of Andress and Saffe (1939) and considered carnallite to be a "*homeotype*" of the hexagonal perovskite structure of $BaTiO_3$ (Burbank and Evans, 1948). He reported the calculated interatomic distances as 0.204 to 0.209 nm for $Mg–H_2O$ and 0.317 to 0.331 nm for K–Cl.

Because of the high *R* factor and the absence of accurate structural details we elected to refine the structure of a natural carnallite crystal. We expected to obtain anisotropic temperature factors, and to locate the hydrogen atoms.

Experimental methods

The crystals used for this study were obtained from the Smithsonian Institute (specimen No. B8605, Wathlingen, near Celle, Hanover, Germany). The sample contained several good prismatic

Table 1. Crystallographic data of carnallite

	Leonhardt (1930)	Andress + Saffe (1939)	Fischer (1973)	Present study
Sp.gr.:	P2/b2/n2$_1$/n	P2/b2/a/n	P2/b2/n2$_1$/n	P2/n2$_1$/n2/a
Z =	12	12	12	12
a =	0.956 nm	0.954 nm	0.9598 nm	1.6119(3) nm
b =	1.605 nm	1.602 nm	1.6141 nm	2.2472(4) nm
c =	2.256 nm	2.252 nm	2.259 nm	0.9551(2) nm

crystals. A single crystal, measuring 0.2 × 0.25 × 0.30 mm, was selected for the investigation. An automated ENRAF-NONIUS CAD4 diffractometer with graphite monochromated MoKα radiation was used for the determination of unit cell parameters and for the collection of intensities. Unit cell parameters were refined by least-squares refinement of the diffraction angles of 24 interplanar spacings. The intensities of over 3,000 diffractions, with theta values ranging from 0.1° to 26.5°, were measured using a θ–2θ scan technique. The 2θ scan width was adjusted for dispersion by the equation, $\theta = (A + B \tan \theta)$, where $A = 0.6$ and $B = 0.35$. A rectangular receiving aperture with variable horizontal width (W in mm $= 4 + \tan \theta$) and constant height (6 mm) was located at 173 mm from the crystal. Each Bragg reflection was scanned for the maximum of 120 seconds. Two-thirds of that time was spent on scanning the peak and one-third to determine the background on the left (LB) and on the right (RB) side of the peak. The measured intensities (I) were scaled as $I = \phi - 2(LB + RB)$. Three peaks

Table 2. Atomic coordinates (standard deviations) and isotropic temperature coefficients

Atoms	x	y	z	B
K(1)	1/4	0	0.2486(1)	3.46(2)
K(2)	0.08860(4)	0.15668(3)	0.74995(7)	3.29(1)
Mg(1)	0.25657(6)	1/4	1/4	1.87(2)
Mg(2)	0.42094(4)	0.08981(3)	0.74770(8)	1.89(1)
Cl(1)	0.23939(5)	1/4	3/4	2.82(2)
Cl(2)	0.16583(4)	0.07525(3)	0.98526(6)	2.86(1)
Cl(3)	0.16928(4)	0.08113(3)	0.48834(6)	2.89(1)
Cl(4)	0.41462(4)	0.08176(3)	0.25235(7)	3.04(1)
Cl(5)	0.01987(4)	0.24957(3)	0.97686(6)	2.94(1)
OW(1)	0.1308(2)	1/4	1/4	3.54(6)
OW(2)	0.3834(1)	1/4	1/4	3.15(5)
OW(3)	0.2554(1)	0.20704(8)	0.4384(2)	3.13(4)
OW(4)	0.2673(1)	0.16936(8)	0.1506(2)	3.57(4)
OW(5)	0.4466(1)	0.01041(7)	0.6500(2)	3.39(4)
OW(6)	0.2967(1)	0.07117(9)	0.7349(2)	3.41(4)
OW(7)	0.4259(1)	0.04662(8)	0.9354(2)	3.26(4)
OW(8)	0.3956(1)	0.16912(8)	0.8444(2)	3.62(4)
OW(9)	0.5448(1)	0.10769(9)	0.7631(2)	3.32(4)
OW(10)	0.4179(1)	0.13155(8)	0.5580(2)	3.48(4)
H(OW1)	0.604(2)	0.250(1)	0.679(3)	* 4.1(6)
H(OW2)	0.412(1)	0.251(1)	0.313(3)	* 4.6(7)
H1(OW3)	0.737(2)	0.173(1)	0.543(3)	* 4.6(7)
H2(OW3)	0.250(2)	0.222(1)	0.505(3)	* 4.3(7)
H1(OW4)	0.734(2)	0.348(1)	0.587(3)	* 4.4(9)
H2(OW4)	0.303(2)	0.345(1)	0.335(3)	* 3.9(6)
H1(OW5)	0.514(2)	0.009(1)	0.326(3)	* 5.1(7)
H2(OW5)	0.417(2)	0.994(1)	0.606(3)	* 3.2(6)
H1(OW6)	0.768(2)	0.072(1)	0.345(3)	* 5.5(8)
H2(OW6)	0.264(2)	0.434(2)	0.682(4)	* 9(1)
H1(OW7)	0.399(2)	0.490(1)	0.568(3)	* 7.2(9)
H2(OW7)	0.422(1)	0.442(1)	0.500(3)	* 2.9(6)
H1(OW8)	0.359(2)	0.317(1)	0.673(3)	* 3.5(6)
H2(OW8)	0.429(2)	0.311(1)	0.623(3)	* 4.3(7)
H1(OW9)	0.565(1)	0.401(1)	0.679(3)	* 2.9(5)
H2(OW9)	0.573(2)	0.104(1)	0.695(3)	* 5.3(7)
H1(OW10)	0.438(2)	0.160(1)	0.561(3)	* 4.7(7)
H2(OW10)	0.411(2)	0.115(1)	0.475(4)	* 8(1)

Isotropic equivalents of anisotropically refined temperature coefficients are defined as:

$$(4/3)\{a^2 B(1,1) + b^2 B(2,2) + c^2 B(3,3)\}$$

* Refined isotropically.

Table 3. Anisotropic temperature coefficients

Atoms	B(1,1)	B(2,2)	B(3,3)	B(1,2)	B(1,3)	B(2,3)
K(1)	3.42(3)	3.67(4)	3.29(3)	-0.09(3)	0	0
K(2)	3.64(3)	2.96(2)	3.26(2)	0.06(2)	-0.09(3)	0.11(2)
Mg(1)	1.86(4)	2.18(4)	1.58(4)	0	0	-0.08(4)
Mg(2)	1.90(3)	2.24(3)	1.52(3)	-0.01(3)	-0.14(3)	-0.07(3)
Cl(1)	2.76(3)	3.36(4)	2.33(3)	0	0	-0.45(4)
Cl(2)	2.94(3)	3.07(3)	2.57(3)	-0.50(2)	0.22(2)	-0.39(2)
Cl(3)	2.95(3)	3.21(3)	2.52(2)	-0.40(3)	-0.39(2)	0.39(2)
Cl(4)	3.61(3)	3.21(3)	2.29(2)	0.39(2)	-0.40(2)	-0.42(2)
Cl(5)	2.71(2)	3.91(3)	2.22(2)	-0.01(3)	-0.23(2)	0.22(2)
OW(1)	1.91(3)	6.6(2)	2.1(1)	0	0	0.2(1)
OW(2)	1.70(9)	5.4(1)	2.3(1)	0	0	-0.3(1)
OW(3)	4.61(9)	3.02(7)	1.75(6)	-0.55(8)	0.04(7)	0.15(7)
OW(4)	3.34(8)	3.16(8)	4.22(9)	0.62(7)	-1.29(8)	-1.52(7)
OW(5)	3.31(8)	2.93(8)	3.94(8)	0.68(7)	-1.14(8)	-1.43(7)
OW(6)	2.08(7)	5.7(1)	2.48(7)	-0.60(7)	-0.13(7)	-0.12(8)
OW(7)	4.88(9)	3.15(8)	1.75(7)	-0.84(7)	-0.33(7)	0.11(6)
OW(8)	3.01(8)	3.23(8)	4.63(9)	0.65(7)	-1.31(8)	-1.50(7)
OW(9)	2.14(7)	5.6(1)	2.27(7)	-0.07(1)	-0.19(7)	0.17(7)
OW(10)	5.3(1)	3.07(8)	2.07(7)	-0.59(8)	-0.45(7)	0.30(7)

Anisotropic temperature coefficients are defined as:

$$\exp\{a^{*2} h^2 B(1,1)+b^{*2} k^2 B(2,2)+c^{*2} l^2 B(3,3)+2a^*b^* hk xB(1,2)+2a^*c^* hl B(1,3)+2b^*c^* klB(2,3)\}$$

were selected and used as intensity standards for monitoring the measurements at 7200 second intervals. The intensities of the standard peaks varied less than 3% during data collection. Because of the known deliquescent nature of carnallite, this small variation of the standards was reassuring. The same standard peaks were used to check the orientation of the crystal (after every 150 intensity measurements). If an angular error of more than 0.07° was observed a new orientation matrix was automatically established by recentering the original 25 diffraction maxima. A total of 3,046 peaks were scanned of which 2,015 ($I \geq 2\sigma$) were considered observed.

Each squared structure factor was assigned a weight, given by $w^{-1} = \{\sigma^2_{counting} + (0.05\ F^2_0)^2\}$. The quantity of $\Sigma\ wF(|F_0| - |F_c|)^2$ was minimized by full matrix least squares refinement. The scattering factors for K, Mg, O and Cl ions were taken from the *International Tables for Crystallography (1974)* and for hydrogen from Stewart et al. (1965). All calculations were done with the CAD4-SDP programs on a PDP11/34 computer. The crystallographic data of carnallite are summarized in Table 1, and the observed and calculated structure factors are given in Table 6.[1]

Fischer's (1973) coordinates of K, Mg, O and Cl ions and their temperature coefficients were refined first with isotropic and later with anisotropic temperature factors. The final R value obtained is 4.86% for all observable (2,015) data. The hydrogen positions and their isotropic temperature coefficients were determined from Fourier difference maps. The refinement cycles were discontinued when the maximum shift over error became less than 0.13. The final unweighted and weighted R factors for 2015 reflections were 0.026 and 0.036, respectively.

Description of the structure

In spite of Fischer's (1973) relatively high discrepancy between observed and calculated intensities ($R = 12.2\%$) his atomic coordinates were confirmed in this study. The difference between corresponding coordinates are less than

[1] To receive a copy of Table 6 order Document No. AM-85-288 from the Business Office, Mineralogical Society of America, 2000 Florida Avenue, N.W., Washington, D.C. 20009. Please remit $5.00 in advance for the microfiche.
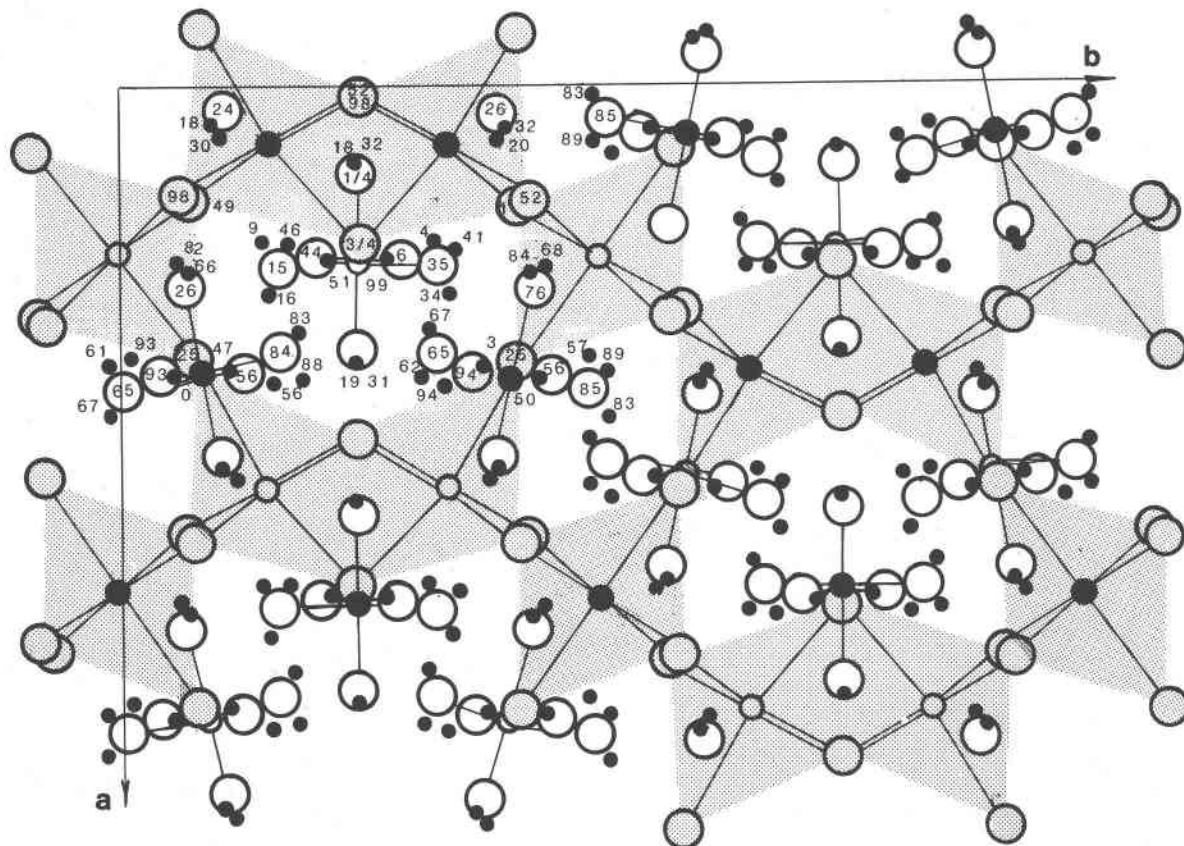
Fig. 1. c-axis projection of the carnallite structure. (Mg medium size, K large dots and circles at or near z = 3/4 and z = 1/4, respectively; Cl small, O large open circles; and H small dots. Elevation (z × 100) shown in first quadrant.

3 percent. As expected, there are more significant changes in the anisotropic temperature coefficients.

Figure 1 illustrates the positions of the atoms in the c-projection of the structure. Figure 2 is a stereoscopic drawing of a unit cell of the structure and illustrates the 3-dimensional network of K–Cl octahedra (shaded) and isolated Mg-water octahedra.

The most unusual features of the carnallite structure are (1) the magnesium's octahedral coordination with neutral water molecules and (2) the unique linkage pattern of the K–Cl octahedra. In the following these two features are discussed in more detail.

1. The water molecules at the corners of the magnesium octahedra act as charge-transfer agents and by increasing the effective cation/anion radius ratio allow twice the number of chlorine anions to coordinate around the magnesium (CN = 12) than the Mg–Cl radius ratio would otherwise allow (CN = 6). The interatomic distances and angles of the isolated Mg octahedra are listed in Table 4a. Both symmetrically distinct octahedra are reasonably regular, although Mg(2) is more distorted.

The average Mg-water distance (0.2045 nm) is shorter than the usual Mg–O distance (0.208 nm). The 0.2045 nm Mg–H_2O distance is not unusual, however. The corresponding distance ranges from 0.2056(1) to 0.2062(1) nm in $Mg(H_2O)_6Cl_2$ (Argon and Busing, 1984). By comparison it is 0.2065(2) nm in $MgSO_4 \cdot 7H_2O$ (Baur, 1964), and 0.204 nm in $Mg(H_2O)S_2O_3$ (Nardelli et al., 1962), and 0.206 nm
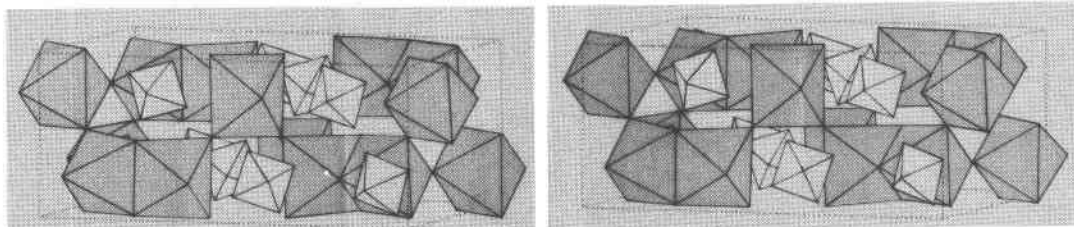

Fig. 2. Stereoscopic drawing of the carnallite structure. (Origin at b/2 of Fig. 1. KCl_6 octahedra shaded, $Mg(H_2O)_6$ octahedra unshaded. Hydrogen not shown.)

Table 4a. Interatomic distances (nm) and angles (°) in $Mg(H_2O)_6$ octahedra

Mg(1) – O(1) = 0.2028(3)	O(1)-Mg(1)-O(2) = 180.00(6)
– O(2) = 0.2045(3)	–O(3) = 89.48(6)
– O(3) = 0.2042(2)	–O(3) = 89.48(6)
– O(3) = 0.2042(2)	–O(4) = 94.83(6)
– O(4) = 0.2053(2)	–O(4) = 94.83(6)
– O(4) = 0.2053(2)	
O(2)-Mg(1)-O(3) = 90.52(6)	O(3)-Mg(1)-O(3) = 178.97(9)
–O(3) = 90.52(6)	–O(4) = 89.46(7)
–O(4) = 85.17(6)	–O(4) = 90.62(7)
–O(4) = 85.17(6)	
O(3)-Mg(1)-O(4) = 89.46(7)	O(4)-Mg(1)-O(4) = 170.34(9)
–O(4) = 90.62(7)	
Mg(2) – O(5) = 0.2056(2)	O(5)-Mg(2)-O(6) = 89.54(8)
– O(6) = 0.2050(2)	–O(7) = 88.71(7)
– O(7) = 0.2040(2)	–O(8) = 179.77(13)
– O(8) = 0.2049(2)	–O(9) = 90.39(8)
– O(9) = 0.2042(2)	–O(10)= 90.07(6)
– O(10) = 0.2041(2)	
O(6)-Mg(2)-O(7) = 89.65(8)	O(7)-Mg(2)-O(8) = 91.48(8)
–O(8) = 90.59(8)	–O(9) = 89.53(8)
–O(9) = 179.18(9)	–O(10)= 178.62(6)
–O(10)= 91.00(6)	
O(8)-Mg(2)-O(9) = 89.49(6)	O(9)-Mg(2)-O(10) = 89.82(6)
–O(10)= 89.74(6)	

in $Mg(SO_4) \cdot 6H_2O$ (Zalkin et al., 1964). A similar metal-water coordination is known for other cations, especially in transition metal hexahydrates, for example, Cr^{3+} (Andress and Carpenter, 1934), Co^{2+} (Mizuno, 1960, and Shchukarev et al., 1963) and Ni^{2+} (Mizuno, 1961, and Kleinberg, 1969).

The interatomic distances and angles around the water molecules are listed in Table 5. The 0.3087(2)–0.3234(2) nm range in H_2O–Cl distances is in reasonable agreement with the corresponding range of 0.3160–0.3499 nm reported for $Mg(H_2O)_6Cl_2$ by Argon and Busing (1984). In $AlCl_3 \cdot 6H_2O$ Buchanan and Harris (1968) found the O–Cl distances to range between 0.302 and 0303 nm, and Mizuno (1960, 1961) found the same distances to average 0.317 nm and 0.322 nm, respectively in $NiCl_2 \cdot 6H_2O$ and in $CoCl_2 \cdot 6H_2O$.

2. The interatomic distances and angles of the two symmetrically non equivalent K–Cl octahedra are listed in Table 4b. Both K–Cl octahedra are distorted, although K(2) is more distorted than K(1). The K–Cl distances (0.294

Table 4b. Interatomic distances (nm) and angles (°) in KCl_6 octahedra

K(1) – Cl(2) = 0.3321(1)	Cl(2)-K(1)-Cl(2) = 81.53(2)
– Cl(2) = 0.3321(1)	–Cl(3) = 94.89(2)
– Cl(3) = 0.3203(1)	–Cl(3) = 175.78(2)
– Cl(3) = 0.3203(1)	–Cl(4) = 90.311(2)
– Cl(4) = 0.3228(1)	–Cl(4) = 87.84(2)
– Cl(4) = 0.3228(1)	
Cl(2)-K(1)-Cl(3) = 175.78(2)	Cl(3)-K(1)-Cl(3) = 88.76(2)
–Cl(3) = 94.89(2)	–Cl(4) = 90.11(2)
–Cl(4) = 87.84(2)	–Cl(4) = 88.99(2)
–Cl(4) = 90.311(2)	
Cl(3)-K(1)-Cl(4) = 88.99(2)	Cl(3)-K(1)-Cl(4) = 178.74(2)
–Cl(4) = 90.11(2)	
K(2) – Cl(1) = 0.3211(1)	Cl(1)-K(2)-Cl(2) = 94.60(2)
– Cl(2) = 0.3154(1)	–Cl(3) = 90.218(2)
– Cl(3) = 0.3289(1)	–Cl(4) = 170.18(2)
– Cl(4) = 0.3271(1)	–Cl(5) = 80.57(2)
– Cl(5) = 0.3206(1)	–Cl(5) = 80.39(2)
– Cl(5) = 0.3218(1)	
Cl(2)-K(2)-Cl(3) = 94.90(2)	Cl(3)-K(2)-Cl(4) = 90.391(2)
–Cl(4) = 90.255(2)	–Cl(5) = 170.45(3)
–Cl(5) = 91.88(2)	–Cl(5) = 87.88(2)
–Cl(5) = 174.37(3)	
Cl(4)-K(2)-Cl(5) = 90.249(2)	Cl(5)-K(2)-Cl(5) = 84.80(2)
–Cl(5) = 90.214(2)	

nm) are within the range of K–Cl distances reported by Wyckoff (1965, p. 555–559) for $K_2HgCl_4 \cdot H_2O$.

The K–Cl octahedra form a 3-dimensional network with large openings, resembling the open frame of the perovskite structure. However, in perovskite the octahedra are linked by sharing only one corner between adjacent octahedra. In carnallite 2/3 of the K–Cl octahedra share faces (that is, have three common corners). The openings around the face-shared octahedra are two octahedra wide and are large enough to accommodate the Mg-water octahedra. Consequently, the carnallite structure is fundamentally different from that of perovskite and the two structures can not be considered isostructural pairs or derivatives.

The cation and water coordination around Cl is also octahedral. There are five different chlorine anions and each is coordinated to two potassium cations and to four water molecules (transmitting the charge of magnesium cations). The Cl–P and Cl–H_2O interatomic distances and angles are listed in Table 4c.

Table 4c. Interatomic distances (nm) and angles (°) in $ClK_2(H_2O)_4$ coordination

Cl(1) – K(2) = 0.3211(1)	K(2)-Cl(1)-K(2) = 81.58(2)
– K(2) = 0.3211(1)	–O(3) = 105.28(4)
– O(3) = 0.3139(2)	–O(3) = 80.203(4)
– O(3) = 0.3139(2)	–O(8) = 160.308(4)
– O(8) = 0.3234(2)	–O(8) = 100.285(4)
– O(8) = 0.3234(2)	
K(2)-Cl(1)-O(3) = 80.203(4)	O(3)-Cl(1)-O(3) = 170.55(5)
–O(3) = 105.28(4)	–O(8) = 91.56(5)
–O(8) = 100.285(4)	–O(8) = 81.06(5)
–O(8) = 160.308(4)	
O(3)-Cl(1)-O(8) = 81.06(5)	O(8)-Cl(1)-O(8) = 77.71(5)
–O(8) = 91.56(5)	
Cl(2) – K(1) = 0.3321(1)	K(1)-Cl(2)-K(2) = 175.12(3)
– K(2) = 0.3154(1)	–O(4) = 75.32(4)
– O(4) = 0.3105(2)	–O(6) = 106.43(4)
– O(6) = 0.3190(2)	–O(7) = 80.215(4)
– O(7) = 0.3149(2)	–O(9) = 78.18(4)
– O(9) = 0.3180(2)	
K(2)-Cl(2)-O(4) = 100.07(4)	O(4)-Cl(2)-O(6) = 90.301(5)
–O(6) = 75.15(4)	–O(7) = 156.46(5)
–O(7) = 100.222(4)	–O(9) = 77.45(5)
–O(9) = 99.39(4)	
O(6)-Cl(2)-O(7) = 99.92(5)	O(7)-Cl(2)-O(9) = 91.47(5)
–O(9) = 168.16(5)	
Cl(3) – K(1) = 0.3203(1)	K(1)-Cl(3)-K(2) = 175.97(3)
– K(2) = 0.3289(1)	–O(3) = 100.280(4)
– O(3) = 0.3188(2)	–O(5) = 100.255(4)
– O(5) = 0.3179(2)	–O(6) = 100.330(4)
– O(6) = 0.3132(2)	–O(9) = 79.86(4)
– O(9) = 0.3186(2)	
K(2)-Cl(3)-O(3) = 80.07(4)	O(3)-Cl(3)-O(5) = 154.56(5)
–O(5) = 74.50(4)	–O(6) = 80.370(5)
–O(6) = 74.06(4)	–O(9) = 89.73(5)
–O(9) = 100.310(4)	
O(5)-Cl(3)-O(6) = 88.51(5)	O(6)-Cl(3)-O(9) = 170.319(5)
–O(9) = 96.73(5)	
Cl(4) – K(1) = 0.3228(1)	K(1)-Cl(4)-K(2) = 176.14(3)
– K(2) = 0.3271(1)	–O(4) = 74.91(4)
– O(4) = 0.3234(2)	–O(5) = 100.213(4)
– O(5) = 0.3188(2)	–O(7) = 80.390(4)
– O(7) = 0.3133(2)	–O(10)= 100.318(4)
– O(10)= 0.3126(2)	
K(2)-Cl(4)-O(4) = 108.31(4)	O(4)-Cl(4)-O(5) = 176.96(5)
–O(5) = 74.63(4)	–O(7) = 84.60(5)
–O(7) = 94.21(4)	–O(10)= 94.30(5)
–O(10)= 78.90(4)	
O(5)-Cl(4)-O(7) = 94.46(5)	O(7)-Cl(4)-O(10)= 170.233(5)
–O(10)= 87.01(5)	
Cl(5) – K(2) = 0.3218(1)	K(2)-Cl(5)-K(2) = 81.53(2)
– K(2) = 0.3206(1)	–O(1) = 111.00(3)
– O(1) = 0.3162(2)	–O(2) = 76.77(2)
– O(2) = 0.3087(2)	–O(8) = 161.17(4)
– O(8) = 0.3193(2)	–O(10)= 78.17(4)
– O(10)= 0.3231(2)	
K(2)-Cl(5)-O(1) = 111.35(3)	O(1)-Cl(5)-O(2) = 168.98(3)
–O(2) = 76.94(2)	–O(8) = 85.15(4)
–O(8) = 100.208(4)	–O(10)= 95.01(4)
–O(10)= 151.19(4)	
O(2)-Cl(5)-O(8) = 85.98(4)	O(8)-Cl(5)-O(10) = 91.21(5)
–O(10)= 78.65(4)	

Table 5. Interatomic distances (nm) and angles (°) around hydrogen

Ions			O – H	H – Cl	O – Cl	O – H – Cl	H – O – H
O(1)	H(1)	Cl(5)	0.80(3)	0.2359(2)	0.3162(1)	177.8(0.2)	114.0(5)
O(2)	H(1)	Cl(5)	0.75(2)	0.2344(2)	0.3087(2)	169.5(0.3)	105.0(5)
O(3)	H(1)	Cl(3)	0.85(3)	0.2347(3)	0.3188(2)	170.2(0.2)	101.9(0.3)
O(3)	H(2)	Cl(1)	0.73(3)	0.2423(3)	0.3139(2)	166.1(0.3)	
O(4)	H(1)	Cl(1)	0.90(3)	0.2267(3)	0.3105(2)	155.0(0.3)	116.8(0.3)
O(4)	H(2)	Cl(4)	0.67(3)	0.2584(2)	0.3234(2)	164.8(0.3)	
O(5)	H(1)	Cl(4)	0.80(3)	0.2396(3)	0.3188(2)	169.6(0.3)	114.2(0.3)
O(5)	H(2)	Cl(3)	0.73(2)	0.2462(2)	0.3179(2)	166.1(0.2)	
O(6)	H(1)	Cl(3)	0.90(3)	0.2254(3)	0.3132(2)	166.2(0.2)	115.2(0.3)
O(6)	H(2)	Cl(2)	0.96(4)	0.2260(4)	0.3190(2)	160.4(0.3)	
O(7)	H(1)	Cl(2)	0.94(3)	0.2231(3)	0.3149(2)	164.7(0.3)	109.6(0.3)
O(7)	H(2)	Cl(2)	0.67(3)	0.2472(3)	0.3133(2)	168.7(0.3)	
O(8)	H(1)	Cl(1)	0.69(2)	0.2547(2)	0.3234(2)	170.6(0.3)	115.1(0.3)
O(8)	H(2)	Cl(5)	0.77(3)	0.2436(3)	0.3193(2)	169.1(0.3)	
O(9)	H(1)	Cl(2)	0.67(2)	0.2516(2)	0.3180(2)	169.2(0.2)	110.6(0.3)
O(9)	H(2)	Cl(3)	0.80(3)	0.2393(3)	0.3186(2)	171.8(0.3)	
O(10)	H(1)	Cl(5)	0.72(3)	0.2548(3)	0.3231(2)	158.5(0.3)	118.0(0.3)
O(10)	H(2)	Cl(4)	0.88(4)	0.2259(4)	0.3126(2)	169.7(0.3)	

Hydrogen bonds the water molecules to Cl anions. The 0.2231(31)–0.2584(25) nm range of the H–Cl distances and the 155.0(26)–177.8(2.4)° range of the O–H–Cl angles are in good correspondence with distances, 0.2206(2)–0.2904(3) nm, and angles, 122.3(2)–179.1(3)°, found by Argon and Busing (1984) in $Mg(H_2O)_6Cl_2$.

Pauling's (1933) principle of electrostatic valency is satisfied in carnallite. Each chlorine anion receives two 1/6 positive charges from potassium and four 1/6 positive charges from magnesium (transmitted through the water molecules). Thus the six 1/6 positive charges of P and Mg balance the −1 valency of Cl.

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