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The Thermal Dehydration of $Cs_3LnCl_6 \cdot 3H_2O$ to Cs_3LnCl_6 (*Ln* = La–Nd) and Their Crystal Structures

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The crystal structure of $Cs_3LaCl_6 \cdot 3H_2O$ has been determined by X ray single crystal analysis. The compound crystallizes from aqueous solution by evaporation at 50°C in the orthorhombic space group *Pnma* ($a = 2124.2(7)$ pm, $b = 865.8(2)$ pm, and $c = 852.3(2)$ pm, $Z = 4$). The coordination polyhedra of lanthanum are slightly *distorted trigonal prisms triply capped by water molecules.* The prisms are connected by common edges forming bent chains $[LaCl_2Cl_{4/2}(H_2O)_3]^-_\infty$. The three different coordination polyhedra around cesium are associated in three dimensions. The compounds with *Ln* = Ce, Pr, and Nd are isotypic. Upon heating these compounds to 130°C they decompose in one step to Cs_3LnCl_6. Cs_3LaCl_6 and Cs_3CeCl_6 crystallize into the Cs_3BiCl_6 type. Cs_3PrCl_6 and Cs_3NdCl_6 belong to another type; its structure was determined from X ray single-crystal data of Cs_3NdCl_6 (space group *Pbcm*, $a = 828.2(2)$ pm, $b = 1322.5(4)$ pm, $c = 2673.0(10)$ pm, $Z = 8$). The $NdCl_6$ octahedra are slightly distorted, and the cesium cations are coordinated with 11 or 8 chlorine atoms. Using the notation of "layers of close-packed octahedra" the stacking frequency is compared with those of the Cs_3BiCl_6, K_3MoCl_6, and Rb_3BiBr_6 types. When annealing the compounds for several days at 280°C they transform irreversibly into the Cs_3BiCl_6 structure.

INTRODUCTION

Oswald and Reller (1) have reported the important role of structural parameters influencing the course of heterogeneous solid-state reactions. They found that the products of thermal decomposition are often metastable. An interpretation of these reactions with regard to kinetical and structural parameters is offered by Stoch (2), which led to a set of empirical principles governing the direction of these processes. Examples of topotactical dehydration of hydrates of ternary fluorides have been presented by Hahn and Massa (3) or Wallis and Bentrup (4).

In the course of our investigations on the existence and the crystal structures of hydrates of ternary alkali metal/lanthanide chlorides we recently reported about the structure of the compounds $Rb_3LnCl_6 \cdot 2H_2O$ (*Ln* = La–Nd) and their thermal behavior (5). These compounds "disproportionate" during the dehydration into RbCl and Rb_2LnCl_5. This is understandable because the compound Rb_3LaCl_6 for instance, becomes thermodynamically stable only above 444°C (6) but the dehydration takes place below 130°C. In the case of cesium as the alkali metal cation we found no analogous dihydrates but trihydrates, i.e., $Cs_3LnCl_6 \cdot 3H_2O$. In this paper we are reporting the crystal structure of these compounds with *Ln* = La–Nd.

According to the remarks on the topotactical reactions mentioned above we additionally investigated the thermal behavior of these hydrates. This was of special interest because of the thermodynamic stability of the anhydrous compounds (6): in contrast to Cs_3LaCl_6, which is thermodynamically metastable below 189°C, the other compounds are all stable at or below their dehydration temperature, as will be shown below. Powder patterns of the dehydration products Cs_3LaCl_6 and Cs_3CeCl_6 could be indexed in the monoclinic Cs_3BiCl_6 type (7) which was found by Seifert et al. (6) for these compounds prepared from the melt. This was not possible in the case of the dehydration products of $Cs_3PrCl_6 \cdot 3H_2O$ and $Cs_3NdCl_6 \cdot 3H_2O$. Thus, we prepared single crystals of Cs_3NdCl_6 from aqueous solution and determined its crystal structure. We found an orthorhombic unit cell with nearly identical cell parameters as for the Cs_3BiCl_6 type, the monoclinic angle excepted. Annealing samples of this type at 280°C for several days leads to the Cs_3BiCl_6 type.

EXPERIMENTAL

Materials. Single crystals of $Cs_3LaCl_6 \cdot 3H_2O$ were prepared by evaporation of a solution of La_2O_3 (99.99%, Johnson Matthey GmbH, Karlsruhe) and CsCl (p.A., Merck, Darmstadt) in hydrochloric acid at 50°C. Single crystals of Cs_3NdCl_6 were prepared by slow evaporation of a solution of Nd_2O_3 (99.99%, Johnson Matthey GmbH, Karlsruhe) and CsCl (p.A., Merck, Darmstadt) in hydrochloric acid at 100°C.

X-ray analysis. Single-crystal data were collected

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with an CAD 4 diffractometer (Enraf Nonius) at ambient temperature (Mo$K\alpha$ radiation, graphite monochromator). Data reduction was performed using the program XCAD4 (8). The structures were solved by SHELX 86 (direct methods) (9), and refinements were done by SHELX 93 (full matrix least squares) (10). The graphics were drawn by SCHAKAL 92 (11). Powder patterns from ambient temperature to 130°C were taken with a Phillips PW 1050/25 goniometer equipped with a proportional counter and a vacuum attachment. During exposure (Cu$K\alpha$ radiation) the samples were under He atmosphere. The digital data were collected and analyzed with PROFIL (12). The calculations were performed with the program LAZY PULVERIX (13). The cell parameters were determined from powder patterns (internal standard, $\alpha - Al_2O_3$) with the least-squares method of Warczewski and de Wolff (14).

Thermoanalytical methods. The thermal behavior of $Cs_3LaCl_6 \cdot 3H_2O$ was observed by means of either the thermal balance TG 750 (Stanton Redcroft) (heating rate, $2\ K \cdot min^{-1}$; purge gas flow, Ar, $6\ ml \cdot min^{-1}$) or the differential scanning calorimeter DSC 7 (Perkin–Elmer) (heating rate, $5\ K \cdot min^{-1}$; purge gas flow, N_2, $10\ ml \cdot min^{-1}$) in the temperature range from 40 to 500°C.

Solution calorimetry. All heats of solution were measured using an isoperibolic underwater calorimeter described elsewhere (15). Molar dilution 1 : 6000, sample masses, 3–7 g. At least three measurements were taken for each compound.

RESULTS OF THE STRUCTURAL INVESTIGATIONS

$Cs_3LaCl_6 \cdot 3H_2O$

To our knowledge no structure of this type is known so far. Information about data collection and analysis of the structure are compiled in Table 1. Atomic positions together with the equivalent thermal parameters for each atom are given in Table 2. In Table 3 main internuclear distances and angles are collected.

The coordination sphere of the lanthanum consists of four C13 and two C12 chloride ions forming a slightly distorted trigonal prism triply capped by water molecules. Thus, the C.N. is 9. The polyhedra are connected by C13–C13 edges with a C13–C13 distance of 341.5 pm. This could be described as an asymmetric double bridge with a bridging angle La–C13–La of 111°. The asymmetry is a result of the two different internuclear distances La–C13. The nearly transstanding polyhedra are forming zigzag chains $[LaCl_2Cl_{4/2}O_3]^-_\infty$ in the [010] direction. Sections of these chains are shown in Fig. 1 together with their arrangment in the unit cell.

The coordination spheres of the three cesium ions in the symmetry independent positions are different. The environment of Cs1 consists of two C11 and four C33 chloride ions and three water molecules. The coordination polyhedra of Cs2 and Cs3 are created from four C11, four C12 chloride ions, and one water molecule. This way the C.N. for each Cs ion is 9. Considering a second oxygen position with a distance of 397.6 pm from Cs3 the C.N. is better

TABLE 1

Experimental Data and Structure Refinement Parameters for $Cs_3LaCl_6 \cdot 3H_2O$ and Cs_3NdCl_6

Formula	$Cs_3LaCl_6 \cdot 3H_2O$	Cs_3NdCl_6
Crystal system	orthorhombic	orthorhombic
Space Group	*Pnma* (no. 62)	*Pbcm* (no. 57)
Lattice parameters (pm) determined at 298 K with 20 reflections	$a = 2124.2(7)$ $b = 865.8(2)$ $c = 852.3(2)$	$a = 828.2(2)$ $b = 1322.5(4)$ $c = 2673.0(10)$
(Volume ($10^6\ pm^3$)	1567.5	2927.7
Number of F.U.	4	8
Calculated density (g/cm^3)	3.38	3.43
Scan-width (ω-scan)	$0.93° \pm (0.48 \tan \theta)°$	$1.2° \pm (0.7 \tan \theta)°$
Collected reflections within	$2121\ (3 < \theta < 26)$ $-21 \leq h \leq 0$ $0 \leq k \leq 8$ $0 \leq l \leq 8$	$6409\ (3 < \theta < 26)$ $-10 \leq h \leq 10|$ $-16 \leq k \leq 0$ $-33 \leq l \leq 0$
Independent reflections with $F_o > 0$	1697	3045
Absorption coefficient (mm^{-1})	10.6	11.9
Absorption correction	semi-empirical (psi scans)	
Number of refined parameters	71	96
Reliability factors[a]	$R = 0.045$ for $F_o < 4\sigma$ $wR2 = 0.138$ for all data GooF = 1.23	$R = 0.054$ for $F_o < 4\sigma$ $wR2 = 0.120$ for all data GooF = 1.00

[a] Definitions of reliability factors: $R = \Sigma \| F_o| - |F_c\| / \Sigma |F_o|$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2] / \Sigma[(wF_o^2)^2]^{1/2}$.

TABLE 2
Atomic Coordinates and Equivalent Temperature Parameters (pm^2) in $Cs_3LaCl_6 \cdot 3\ H_2O$

Atom	x/a	y/b	z/c	U_{eq}[a]
La	0.55257(3)	0.25	−0.0007(1)	0.0160(3)
Cs1	0.46162(4)	0.25	0.5256(1)	0.0281(3)
Cs2	0.76646(5)	0.25	0.2623(1)	0.0325(3)
Cs3	0.75974(4)	0.25	0.7569(1)	0.0292(3)
C11	0.3370(1)	−0.0091(3)	0.4981(2)	0.0286(5)
C12	0.6581(1)	0.4687(3)	1.0163(3)	0.0279(5)
C13	0.4857(1)	0.0276(2)	0.1946(2)	0.0245(5)
O1	0.5984(5)	0.25	0.7231(11)	0.029(2)
O2	0.5949(5)	0.25	0.2835(11)	0.032(2)
O3	0.4353(4)	0.25	0.9077(12)	0.029(2)

Note. Further information of the structure determination is available at Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, 76344 Eggenstein-Leopoldshafen 2, with specification of the identification number CSD401032, the authors, and the citation of the journal.

[a] $U_{eq} = 1/3[U_{11} + U_{22} + U_{33}]$ (28).

described as (9 + 1). The polyhedra are sharing edges, corners, and faces which leads to a three-dimensional network.

Powder patterns of the compounds with *Ln* = Ce–Nd could be indexed within this structure type. In Table 4 the unit cell parameters of these compounds are collected.

Cs_3NdCl_6

To our knowledge this type of crystal structure is not known either. It is a distortional variant of the cubic elpasolite. Information about data collection and analysis of the structure are given in Table 1. Atomic positions together with the equivalent thermal parameters for each atom are collected in Table 5.

Like in other structure types which can be derived from the cubic elpasolite, slightly distorted isolated octahedra are present in Cs_3NdCl_6. Since there are two atomic positions for Nd two different octahedra exist. They are notably rotated from their ideal positions. The distorted octahedron around Nd1 consists of atoms C11, C12, two C13, and two C16. The angles for Cl–Nd1–Cl range from 83.8° to 98.7° for the small octahedron angles and from 177.6° (two times) to 178° for the large ones. Two C14 atoms, two C15, and two C17 make up the octahedron around Nd2. The range of the angles is smaller: 84.5° to 93.7° and 174.8° (C14–Nd2–C15) to 175.8° (C17–Nd2–C17). The environments of the cesium ions are composed of 8 (two times) and 11 chloride ions which have distances partially longer than 400 pm. In Table 6 the internuclear distances are given. Thus, the structure may be seen as distorted octahedra around Nd with the Cs ions acting as bulky counterions. This view is supported by a comparison of the measured radii with the corresponding Shannon radii (16), which show smaller values for the Nd coordination centers and larger ones for the Cs ions.

THERMAL BEHAVIOR

$Cs_3LaCl_6 \cdot 3H_2O$ was dehydrated by annealing at 130°C for 1 hr. The powder pattern taken at ~130°C could be indexed in the Cs_3BiCl_6 type and the following cell parameters were calculated (in comparison with those at ambi-

TABLE 3
Interatomic Distances (pm) with ESDs in $Cs_3LaCl_6 \cdot 3\ H_2O$

La–O1 (a)	254.7(9)	Cs2–C12 (h,i)	349.2(2)
La–O2	258.4(9)	Cs2–C12 (j,k)	363.1(2)
La–O3 (a)	261.1(9)	Cs2–C12 (a,c)	364.4(2)
La–C13 (b)	291.5(2)	Cs2–O2	364.9(11)
La–C12 (a,c)	293.9(2)	Cs2–C11 (f,g)	365.4(2)
La–C13 (d,e)	302.8(2)		
Cs1–O3	330.4(10)	Cs3–O1	344.0(10)
Cs1–O1	335.8(10)	Cs3–C11 (l,m)	347.6(2)
Cs1–C13 (b)	345.4(2)	Cs3–C12 (b)	362.4(2)
Cs1–C11 (b)	347.8(3)	Cs2–C12 (j,k)	363.0(2)
Cs1–O2	350.3(11)	Cs3–C11 (f,g)	364.6(2)
Cs1–C13 (f,g)	356.6(2)	Cs3–O3 (n)	398.4(11)

Coding of equivalent positions

(a) $x, y, z - 1$
(b) $x, -y + 1/2, z$
(c) $x, -y + 1/2, z - 1$
(d) $-x + 1, -y, -z$
(e) $-x + 1, y + 1/2, -z$
(f) $-x + 1, -y, -z + 1$
(g) $-x + 1, y + 1/2, -z + 1$
(h) $x + 1/2, y, -z + 1/2$
(i) $x + 1/2, -y + 1/2, -z + 1/2$
(j) $-x + 3/2, y - 1/2, -z + 3/2$
(k) $-x + 3/2, -y + 1, z - 1/2$
(l) $x + 1/2, y, -z + 3/2$
(m) $x + 1/2, -y + 1/2, -z + 3/2$
(n) $-x + 3/2, -y + 1, z + 1/2$

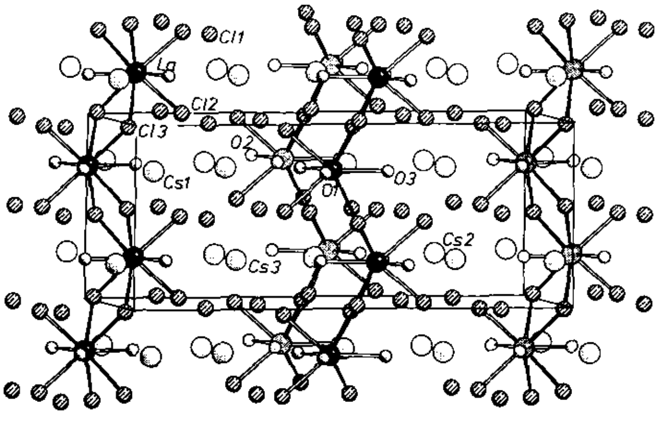

FIG. 1. Sections of the anionic chains $[LaCl_2Cl_{4/2}O_3]_x^-$ in $Cs_3LnCl_6 \cdot 3H_2O$ and their arrangement in the unit cell.

ent temperature (6)) for Cs_3LaCl_6: a = 2748.7(8) pm (2728.6(5) pm), b = 827.1(5) pm (829.1(1) pm), c = 1364.3(6) pm (1330.5(2) pm), and β = 100.38(4)° (99.64(1)°). The anhydrous compound rehydrates at ambient temperature for 1 day to $Cs_3LaCl_6 \cdot 3H_2O$. Measurements with the thermal balance and DSC shows that the dehydration takes place in one step. Following the dehydration by DSC, calibrated on recommendations of the GEFTA (17), the reaction starts at 102°C. The reaction enthalpy was determined to be 248 J/g from these measurements. Substracting the heat of vaporization of water leaves 77 kJ/mol for the elimination of the crystal water. This is in excellent agreement with the measurements of the heats of solution at 25°C: $Cs_3LaCl_6 \cdot 3H_2O$, 14.0(3) kJ/mol; Cs_3LaCl_6, −64.8(4) kJ/mol. The difference of the heats of solution at 25°C is thus 78 kJ/mol.

This leads to a value of 26 kJ/mol for the elimination of one water molecule from $Cs_3LaCl_6 \cdot 3H_2O$. Investigations of hydrates of cerium(III) chlorides have yielded a value of 15 kJ/mol for each water molecule (18).

The dehydration of the isotypic compounds with *Ln* = Ce–Nd takes place in the same temperature range. The poor quality of the powder patterns taken from products of the dehydration of $Cs_3LnCl_6 \cdot 3H_2O$ (*Ln* = Ce and Pr) did not permit accurate determination of their cell parameters, but the strongest reflections could best be indexed in the Cs_3BiCl_6 type (Cs_3CeCl_6) and the Cs_3NdCl_6 type (Cs_3PrCl_6). The poor quality of the powder patterns manifested itself in broadened reflections. This may be due to the two crystal forms of the anhydrous compounds with very similar powder patterns in the samples during the measurements. Residual crystal water in the powders while taking the powder patterns could be exclosed.

TABLE 4

Lattice Parameters for $Cs_3LnCl_6 \cdot 3H_2O$ (Ln = La − Nd) Obtained from Powder Patterns

	a [pm]	b [pm]	c [pm]	V_{mol} [$cm^3 * mol^{-1}$]
$Cs_3LaCl_6 \cdot 3H_2O$	2123.7(6)	868.2(2)	854.2(4)	237.3(2)
$Cs_3LaCl_6 \cdot 3H_2O$	2112.3(6)	863.6(2)	852.7(4)	234.1(2)
$Cs_3LaCl_6 \cdot 3H_2O$	2108.3(6)	863.8(2)	846.6(4)	232.1(2)
$Cs_3LaCl_6 \cdot 3H_2O$	2103.5(6)	861.4(2)	843.8(4)	230.2(2)

Seifert *et al.* found the following temperatures from emf measurements for the reactions CsCl + Cs_2LnCl_5 = Cs_3LnCl_6 (6). Below these temperatures the low-temperature modification of the anhydrous compounds in the Cs_3BiCl_6 type becomes thermodynamically metastable: Cs_3LaCl_6, 189°C, Cs_3CeCl_6, 10°C; and Cs_3PrCl_6, −130°C.

DISCUSSION

Chains of edge-connected polyhedra as in $Cs_3LaCl_6 \cdot 3H_2O$ are not unusual in complex water-containing lanthanide(III)-chlorides. Anionic chains of triply capped trigonal prisms with C.N. 9 for lanthanum are present in $CsLaCl_4 \cdot 3H_2O$ (19) ($CsUCl_4 \cdot 3H_2O$ type (20)) and $(CH_3NH_3)_3LaCl_6 \cdot 3H_2O$ (21). Face-connected neutral chains of triply capped prisms were found in $LaCl_3 \cdot 3H_2O$ (22). In compounds of the lighter lanthanoide ions the C.N. 8 was observed in accordance to their decreasing ionic radii. Examples for this are $(CH_3NH_3)_8[NdCl_6][NdCl_4(H_2O)_2]_2Cl_3$ (23), $(CH_3NH_3)_3PrCl_6 \cdot 2H_2O$ (24), and $CeCl_3 \cdot 3H_2O$ (18). Interestingly,

TABLE 5

Atomic Coordinates and Equivalent Temperature Parameters (pm^2) in Cs_3NdCl_6

ATOM	x/a	y/b	z/c	U_{eq}[a]
Nd1	0.2590(1)	0.0824(1)	0.75	0.0248(3)
Nd2	0.2118(1)	−0.25	0.5	0.0258(3)
Cs1	−0.1820(1)	0.2562(1)	0.8369(1)	0.0373(3)
Cs2	−0.2636(2)	−0.0868(1)	0.4499(1)	0.0688(5)
Cs3	−0.3091(1)	−0.0924(1)	0.6526(1)	0.0340(3)
C11	0.1256(7)	0.2715(4)	0.75	0.033(1)
C12	0.4035(7)	−0.1033(4)	0.75	0.038(1)
C13	0.4552(5)	0.1380(3)	0.6734(2)	0.048(1)
C14	−0.0315(5)	−0.1775(4)	0.5583(2)	0.049(1)
C15	0.4390(5)	−0.1609(3)	0.5584(2)	0.051(1)
C16	0.0530(5)	0.0244(3)	0.6764(2)	0.053(1)
C17	0.2244(7)	−0.0838(3)	0.4426(2)	0.059(1)

Note. Further information of the structure determination are available at Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, 76344 Eggenstein-Leopoldshafen 2, with specification of the identification number CSD 401033, the authors, and the citation of the journal.

[a] $U_{eq} = 1/3[U_{11} + U_{22} + U_{33}]$ (28).

TABLE 6

Interatomic Distances (pm) with ESDs in Cs_3NdCl_6

Nd1–Cl6(a)	271.5(4)	Nd2–Cl7 (b)	268.2(4)
Nd1–Cl3 (a)	271.6(4)	Nd2–Cl5 (b)	271.4(4)
Nd1–Cl2	273.2(5)	Nd2–Cl4 (b)	272.1(4)
Nd1–Cl1	273.4(5)	Average	270.6
Average	272.1		
Cs1–Cl3 (c)	339.8(4)	Cs2–Cl5 (f)	359.0(5)
Cs1–Cl4 (d)	342.7(5)	Cs2–Cl7 (f)	366.8(5)
Cs1–Cl1	345.4(4)	Cs2–Cl4 (b)	366.9(5)
Cs1–Cl2 (d)	349.5(4)	Cs2–Cl4	367.9(5)
Cs1–Cl7 (e)	364.8(5)	Cs2–Cl3 (f)	371.8(5)
Cs1–Cl6 (a)	364.9(5)	Cs2–Cl6 (f)	388.8(5)
Cs1–Cl5 (d)	368.3(5)	Cs2–Cl5 (g)	393.0(5)
Cs1–Cl6 (d)	372.1(5)	Cs2–Cl7	404.7(6)
Average	355.9	Cs2–Cl5 (h)	415.3(5)
		Cs2–Cl7 (g)	424.5(6)
Cs3–Cl5 (g)	339.3(5)	Cs2–Cl4 (f)	427.1(5)
Cs3–Cl6	343.2(4)	Average	389.6
Cs3–Cl1 (i)	351.1(4)		
Cs3–Cl7 (f)	352.1(4)		
Cs3–Cl2 (g)	353.0(4)		
Cs3–Cl4	359.3(4)		
Cs3–Cl3 (g)	366.1(5)		
Cs3–Cl3 (j)	380.6(5)		
Average	355.6		

Coding of equivalent positions

(a) $x, y, -z + 3/2$
(b) $x, -y - 1/2, -z + 1$
(c) $x - 1, y, -z + 3/2$
(d) $-x, y + 1/2, -z + 3/2$
(e) $-x, -y, z + 1/2$
(f) $-x, -y, -z + 1$
(g) $x - 1, y, z$
(h) $x - 1, -y - 1/2, -z + 1$
(i) $-x, y - 1/2, -z + 3/2$
(j) $-x, y - 1/2, z$

$Cs_3NdCl_6 \cdot 3H_2O$ is the first water-containing chloride with the C.N. 9 for Nd.

The thermal dehydration of the trihydrates leads to distortional variants of the cubic elpasolites A_2BMX_6 (space group $Fm\bar{3}m$). In literature two different ways are given to describe such distortional variants. The more common one was recently discussed in detail by Mattfeld and Meyer (25): close-packed layers of AX_3 with partially occupied octahedral sites are stacked with different frequencies along their stacking axis. This is symbolically described as . . . (103) (010) (103) (010) . . . in the cubic elpasolite, where (103) means a layer consisting of 1 × A, 0 × B / 0 × M, and 3 × X. In distortional variants layers of other compositions are inserted in the stacking frequency. In this notation the sequence of the layers in Cs_3NdCl_6 can be described as . . . (103) (010) (103) (000) (202) (012) (202) . . . which is illustrated in Fig. 2. This sequence is exactly what Mattfeld and Meyer found for the Cs_3BiCl_6 type; thus it is not possible to distinguish between the two types.

In this description the existence of planar (or nearly so) layers is assumed. This is not necessary in the second

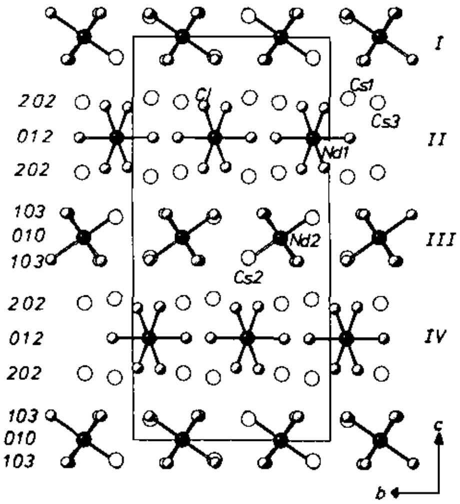

FIG. 2. Projection of the layer sequence in Cs_3NdCl_6: left-hand side, notation from Mattfeld and Meyer; right-hand side, labels of the layers of close-packed octahedra.

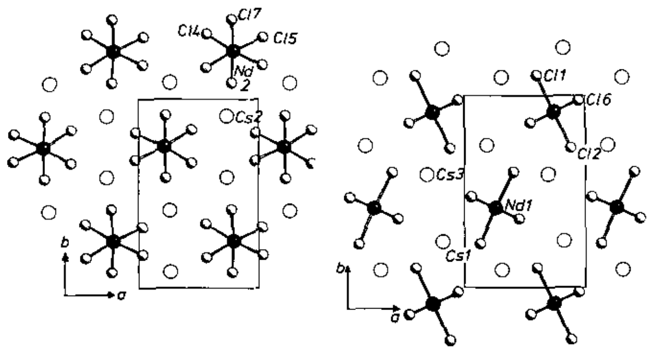

FIG. 3. Arrangement of the octahedra of the two different layers in (*a*, *b*) planes in Cs_3NdCl_6.

description elaborated by Benachenhou *et al.* (7) considering MX_6 octahedra as entities. In this case layers of octahedra can be defined. The octahedra could be rotated from their ideal positions with respect to each other. The stacking sequence and the arrangement of the octahedra in these layers are the criteria to distinguish between distortional variants of the cubic elpasolite.

Projections of the structure of Cs_3NdCl_6 in two (*a*, *b*) planes are depicted in Fig. 3. They show the arangement of the octahedra in the two different layers. The grouping of the octahedra in the layers is identical with that found in (*b*, *c*) planes of Cs_3BiCl_6 (7).

A projection normal to these planes which is the stacking direction of the octahedra planes is illustrated in Fig. 3. It shows the existence of two different types of layers: (a) layers containing only octahedra viewed along a "threefold" axis and (b) layers with octahedra viewed along a "twofold" axis. That is what Benachenhou *et al.* (7) considered for Cs_3BiCl_6, Rb_3BiBr_6 (26), and K_3MoCl_6 (27) in their stacking directions. As in Rb_3BiBr_6 the stacking sequence is repeated after four layers (labeled I–IV in Fig. 2) in comparison with a 12-layer frequency in Cs_3BiCl_6 and a 6-layer frequency in K_3MoCl_6. In this manner it is conceivable to view the structure of Cs_3NdCl_6 given here as a "mixture" of the Cs_3BiCl_6 and the Rb_3BiBr_6 types. But in contrast to the three compared types the octahedra viewed along the twofold axis of layers I and III (Fig. 2) are orientated in the same direction. The direction of this orientation alternates between the layers. In Cs_3BiCl_6, Rb_3BiBr_6, and K_3MoCl_6 the orientation of these octahedra alternates with respect to each other in the same layer.

With the existence of this structure type one question still remains: is this structure type either

(a) The "lowest" temperature modification of Cs_3NdCl_6 not observed from the melt for kinetical reasons or

(b) A metastable state formed in the course of a heterogeneous solid-state reaction by means of the considerations of Oswald and Reller or Stoch?

This question will be addressed by further investigations by means of DSC measurements and solution calorimetry.

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