Preparation and Crystal Structure of $Ln_3VO_4Cl_6$ (Ln = La, Ce, Pr, Nd)

H. Kämmerer and R. Gruehn[1]

Institut für Anorganische und Analytische Chemie der Justus-Liebig-Universität, Heinrich-Buff-Ring 58, D-35392 Giessen, Germany

The new compounds $Ln_3VO_4Cl_6$ (Ln = La, Ce, Pr, Nd) were prepared by heating a mixture of LnCl$_3$, LnOCl, and V_2O_5 (3:3:1) in evacuated, sealed silica ampoules (850°C, 5 d). Single crystals of the lanthanum compound could be obtained by chemical vapor transport (900 → 800°C; 10 d; transport agent Cl$_2$, p{298 K} = 1 atm). The single-crystal study showed that $La_3VO_4Cl_6$ crystallizes in the hexagonal space group $P6_3/m$ (No. 176), (Z = 2), with a = 12.5346(9) Å and c = 4.1331(4) Å (diffractometer data). Least-squares refinement based on 618 unique reflections led to a conventional R value of 1.49% for all data. Vanadium is tetrahedrally coordinated ($d_{(V–O)}$ = 1.72–1.75 Å). For lanthanum, a C.N. = 10 (3 × O {$d_{(La–O)}$ = 2.44–2.98 Å}, 7 × Cl {$d_{(La–Cl)}$ = 2.95–3.12 Å}) was found. Apart from the smaller coordination number of V^{5+} as compared to Nb^{5+}, the structure is closely related to that of $Pr_3NbO_4Cl_6$. © 1996 Academic Press, Inc.

1. INTRODUCTION

A number of compounds in the systems Ln/M^{5+}/O/Cl (Ln = La–Tb; M^{5+} = Nb^{5+}, Ta^{5+}) are well characterized (Table 1), while for M = V only compounds of two different stoichiometries (La$_3$VO$_4$Cl$_5$ (21) and perhaps LnVO$_3$Cl {Ln = La-Lu} (22)) are known so far. Compounds in the systems Ln/M^{5+}/O/Cl often have quite similar structures for niobium as well as for tantalum so that compounds that exist for tantalum are frequently also found for niobium with only minor structural deviations (Table 1, types 1–5). The relationship between vanadium on the one hand and niobium and tantalum on the other is rarely pronounced. Surprisingly, in our investigations on systems Ln/V/O/Cl (Ln = La–Lu) we obtained the new oxochlorovanadates $Ln_3VO_4Cl_6$ (Ln = La–Nd), which are closely related to the Pr$_3$NbO$_4$Cl$_6$ structure type (6). Their synthesis, crystal growth, and crystal structure is described here.

[1] To whom correspondence should be addressed. E-mail: Gruehn@sp10ac.anorg.chemie.uni-giessen.de.

2. EXPERIMENTAL AND RESULTS

2.1. Preparation

Starting materials. We used V$_2$O$_5$ (puriss >99.9%, Fluka AG), LaCl$_3$ · 7H$_2$O (puriss >99.0%, Fluka AG), CeCl$_3$ · 7H$_2$O (purum >98.5%, Fluka AG), PrCl$_3$ · 7H$_2$O (puriss >99.9%, Johnson Matthey), NdCl$_3$ · 6H$_2$O (puriss >99.9%, Fluka AG), La$_2$O$_3$ (purum >99%, Fluka AG), Pr$_2$O$_3$ (by reduction of Pr$_6$O$_{11}$ {puriss >99.9%, Fluka AG} in a flow of hydrogen {16 h, 800°C}), Nd$_2$O$_3$ (puriss >99.9%, Fluka AG), LaOCl (by heating of LaCl$_3$ · 7H$_2$O {20 h, 650°C} in a flow of nitrogen), CeOCl (by heating of CeCl$_3$ · 7H$_2$O {2 h, 150°C, followed by rapid heating in a flow of N$_2$ to 600°C, 3 h}), PrOCl and NdOCl (by heating of PrCl$_3$ · 7H$_2$O and NdCl$_3$ · 6H$_2$O in a flow of N$_2$ {20 h, 600°C}), and Cl$_2$ (purity >99.8%, Messer-Griesheim).

For the *preparation of $Ln_3VO_4Cl_6$* (Ln = La, Pr, Nd) we used two different methods: (a) A mixture of LnCl$_3$ · 7(6)H$_2$O, LnOCl, and V$_2$O$_5$ (3:3:1) was homogenized and heated carefully (to 280°C with 1°/min) under a dynamic vacuum in order to dehydrate it. Then the mixture was heated in evacuated, sealed silica ampoules (La: 850°C, 5 d; Pr: 850°C, 10 d; Nd: 800°C, 9 d). The powder pattern of the light-blue products (small amounts of V^{4+}, but influenced by the presence of Pr or Nd) showed only reflections of Ln$_3$VO$_4$Cl$_6$. (b) Single-phase, light-blue $Ln_3VO_4Cl_6$ (Ln = La, Pr, Nd) can also be obtained from stoichiometric mixtures (1:2) of LnVO$_4$ (from Ln_2O$_3$ and V$_2$O$_5$; 840°C, 72 h) and LnCl$_3$ (dehydration of LnCl$_3$ · 7(6)H$_2$O in a preliminary step as in (a)) by heating (800°C, 6 d) in evacuated silica ampoules.

Light-blue, probably oxygen-deficient La$_3$VO$_4$Cl$_6$ could be oxidized with chlorine (Cl$_2$, p{298 K} = 1 atm) by heating (850°C, 2 d) in silica ampoules. The light-yellow product (now fully oxidized) of this process may be used immediately for the following experiments. For crystallization, the ampoule was subjected to a chemical transport reaction (23) in a temperature gradient (T_2 → T_1, T_2 = 900°C, T_1 = 800°C). In this case yellow single crystals of La$_3$VO$_4$Cl$_6$ could be obtained.

TABLE 1

Compounds in the Systems $Ln/M^{5+}/O/Cl$ (Ln = La–Tb; M^{5+} = Nb^{5+}, Ta^{5+}) (1,2)

No.	Ln/Nb^{5+}/O/Cl	Ln/Ta^{5+}/O/Cl
1	$Ln_3NbO_4Cl_6$ Ln = La (2, 3), Ce (4, 5), Pr (3, 5, 6), Nd (5)	$Ln_3TaO_4Cl_6$ Ln = La (3, 7), Ce (7), Pr (8), Nd (7)
2	$Ln_2NbO_4Cl_3$ Ln = La (2, 4, 9), Ce (2, 4)	$Ln_2TaO_4Cl_3$ Ln = La, Ce (7, 10)

3[a]	$Ln_2A^{4+}NbO_6Cl_3$
	 Ln = La, Ce; A^{4+} = Ce (4); A^{4+} = Th, U (11);
	 Ln = Pr, Nd; A^{4+} = Ce, Th, U (5);
	 Ln = Sm − Tb; A^{4+} = Th (11)
		$Ln_2A^{4+}TaO_6Cl_3$[b]
		 Ln = La, Pr, Nd; A^{4+} = Ce (12); Ln = Ce;
		  A^{4+} = Ce (12, 13); Ln = Sm; A^{4+} = Ce (14);
		 Ln = La; A^{4+} = Th (13); Ln = Ce, Pr, Nd, Sm;
		  A^{4+} = Th (14); Ln = La–Sm; A^{4+} = U (14)

4	$Ln_2Ce_x^{3+}Ce_{1-x}^{4+}NbO_6Cl_{3-x}$ Ln = La, Ce (4)	$Ln_2Ce_x^{3+}Ce_{1-x}^{4+}TaO_6Cl_{3-x}$ Ln = La (12, 15), Ce (12), Nd (14)
5[a]	$Ln_3NbO_5XCl_3$ X = OH; Ln = La (4), Ce, Pr, Nd (5); X = F; Ln = La (4), Ce, Pr, Nd (5)	$Ln_3TaO_5XCl_3$ X = OH; Ln = La (7, 8, 12, 13), Ce (12), Pr (8, 13), Nd (13) X = F; Ln = La (7, 13)
6	$LnNb_2O_6Cl$ Ln = La (2, 4, 9, 16), Ce (4)	
7		$Ln_2Ta_2O_7Cl_2$ Ln = Pr (17), Nd (2, 17, 18), Sm (19)
8		$Nd_{7.33}Ta_8O_{28}Cl_6$ (2, 18)

[a] Near-related compounds were (No. 3) Ln^{3+} is partially substituted by Ln^{4+} or An^{4+}, respectively, (No. 5) O^{2-} is partially substituted by X^- (OH$^-$, F$^-$).

[b] In systems with U isostructural compounds $Ln_3UO_6Cl_3$ (Ln = La, Pr, Nd) (20) can be formed.

Preparation of $Ce_3VO_4Cl_6$. A mixture of CeCl$_3$, CeOCl, and V$_2$O$_5$ (3:3:1) was homogenized and heated in sealed silica ampoules (850°C, 5 d), after the dehydration process described in (a). The powder pattern of the light-brown product showed only reflections of $Ce_3VO_4Cl_6$. Efforts to obtain single crystals of $Ce_3VO_4Cl_6$ by chemical transport using chlorine (Cl$_2$, p{298 K} = 1 atm) as transport agent have failed so far. Our experiments revealed only the chemical transport of CeVO$_4$ under these conditions.

Single crystals of $Ln_3VO_4Cl_6$ (Ln = La, Ce, Pr, Nd) could be obtained by chemical transport reaction ($T_2 \rightarrow T_1$, T_2 = 850°C, T_1 = 750°C) from the starting material $Ln_3VO_4Cl_6$ without addition of a transport agent in evacuated, sealed silica ampoules.

2.2. X-Ray Studies

Lattice parameters for $Ln_3VO_4Cl_6$ (Ln = La-Nd) were derived from Guinier powder data (Cu$K\alpha_1$, quartz mono-
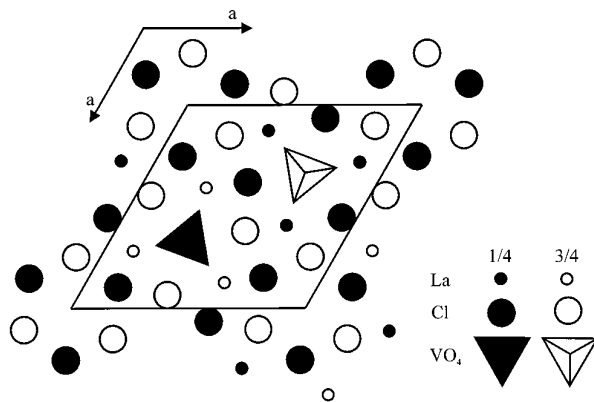
TABLE 2

$Ln_3VO_4Cl_6$: Lattice Parameters with Standard Deviations (Guinier Data)

Compound	a(Å)	c(Å)	V(Å^3)
La$_3$VO$_4$Cl$_6$	12.5314(10)	4.1330(5)	562.07(11)
Ce$_3$VO$_4$Cl$_6$	12.4811(17)	4.0796(7)	550.36(18)
Pr$_3$VO$_4$Cl$_6$	12.4568(13)	4.0170(4)	539.81(13)
Nd$_3$VO$_4$Cl$_6$	12.4381(12)	3.9726(4)	532.24(12)

FIG. 1. Structure model of La$_3$VO$_4$Cl$_6$ along [001] (ATOMS-Plot[33]); z parameters are given for La, Cl as well as for O1 of the VO$_4$ polyhedra.

TABLE 3
La₃VO₄Cl₆: Crystallographic Data

Crystal system	Hexagonal
Space group	$P6_3/m$ (No. 176)
Crystal shape and color	Hexagonal prisms, light-yellow
Cell parameters (diffracto-meter data)	$a = 12.5346(9)$ Å $c = 4.1331(4)$ Å
Cell volume	562.38 Å³
Density (diffractometer)	4.40 g/cm³
Formula units Z	2
Mole volume	281.19 Å³
Crystal dimensions	$(0.30 \times 0.09 \times 0.07)$ mm
μ(Mo$K\alpha$)	133.7 cm⁻¹
$F(0\,0\,0)$	656
Diffractometer	AED-2 (Siemens/Stoe)
Radiation, monochromator, scan mode	Mo$K\alpha$, graphite, ω-scan
Range of 2θ	$3° \leq 2\theta \leq 60°$
Corrections of intensities	Lorentz and polarization correction, numerical, ψ-scan
Recorded reflections	6548
h, k, l range	$-17 \leq h, k \leq 17; -5 \leq l \leq 5$
Unique reflections	618 (597 with $F_o \geq 4\sigma\,F_o$)
Solution and refinement	Patterson, full-matrix least-squares, scattering factors (28, 29)
Free parameters	31
R(int)	0.0521
$R(|F|)$	0.0149
$R(|F|)(F_o > 4\sigma\,\{F_o\})$	0.0141
$wR(F^2)^a$	0.037
Goodness of fit S	1.231
Residual electron density (max, min)	$+0.86\ e/\text{Å}^3/-1.61\ e/\text{Å}^3$

$$^a\ w = \frac{1}{[\sigma^2(F_o^2) + (0.0129 \cdot P)^2 + 0.60 \cdot P]},\ \text{with } P = \frac{(\text{Max}(F_o^2) + 2 \cdot F_c^2)}{3}.$$

FIG. 2. Coordination of La in La₃VO₄Cl₆ (ORTEP[34] plot showing 95% probability displacement ellipsoids).

the remaining atoms. It should be noted that the vanadium atoms occupy split positions when choosing a disorder model for the structure description as listed below. Refinement of positional and anisotropic displacement parameters for all atoms gave a conventional discrepancy factor $R(|F|) = 1.41\%$ and $wR(F^2) = 3.73\%$. The final positional and thermal parameters are listed in Table 4

chromator, $\lambda = 1.54051$ Å, low-quartz as internal standard) using the computer program SOS (24). The correct assignment of (hkl) indices was checked by comparing observed diffraction angles and intensities with those from LAZY-PULVERIX (25) calculations on the basis of the single-crystal data. The lattice parameters for $Ln_3VO_4Cl_6$ (Ln = La-Nd) are reported in Table 2.

A single crystal of La₃VO₄Cl₆ was selected for measurement on a 4-circle diffractometer. Preliminary search techniques confirmed the hexagonal lattice with $a = 12.5346(9)$ Å, $c = 4.1331(4)$ Å, with systematic absences compatible to the space group $P6_3/m$ (No. 176). A total of 6548 reflections were collected. After correction of Lorentz and polarization effects, merging yielded 618 unique reflections (R(int) = 0.0521) (Table 3).

The lanthanum atoms were located from a three-dimensional Patterson function (26). A full matrix least-squares refinement was carried out (27) using atomic scattering factors from Cromer et al. (28, 29), giving the positions of
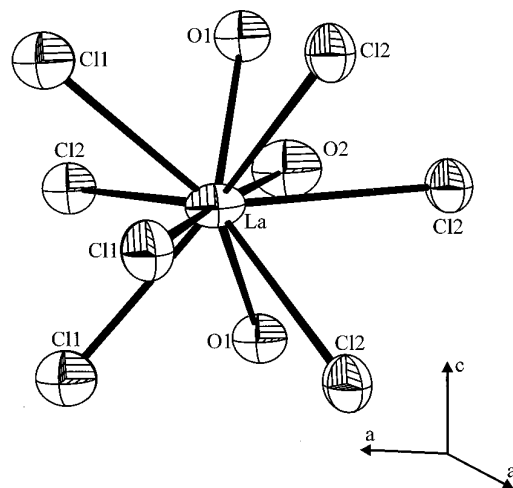

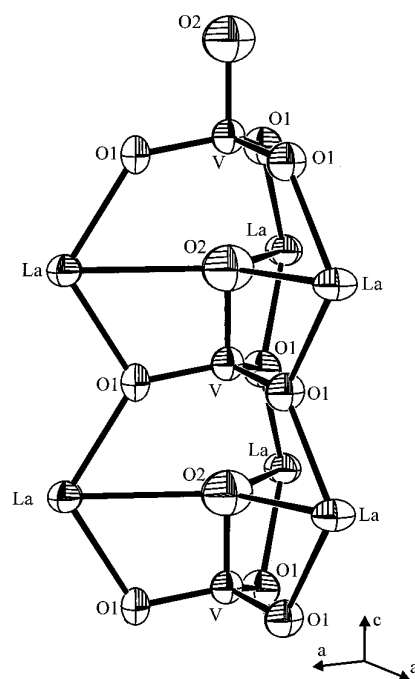**FIG. 3.** Coordination of V in La₃VO₄Cl₆ ([La₃VO₄]⁶⁺ polyhedra) (ORTEP[34] plot showing 95% probability displacement ellipsoids).

TABLE 4
La₃VO₄Cl₆: Positional Parameters (Standard Deviations in Brackets)

Atom	Wyckoff position	x	y	z	S.O.F.	$B_{eq.}$
La	$6h$	0.40731(2)	0.12517(2)	1/4	0.5	0.940(6)
V	$4f$	2/3	1/3	0.32680(25)	0.16667	0.755(21)
Cl(1)	$6h$	0.25271(6)	0.14922(7)	3/4	0.5	1.143(11)
Cl(2)	$6h$	0.44484(6)	0.37887(6)	1/4	0.5	1.038(11)
O(1)	$6h$	0.52121(19)	0.21265(19)	3/4	0.5	1.000(30)
O(2)	$2d$	2/3	1/3	1/4	0.16667	1.682(65)

and 5, interatomic distances and angles are found in Table 6 and 7.

3. DESCRIPTION AND DISCUSSION

A view of the crystal structure of $La_3VO_4Cl_6$ along [001] is shown in Fig. 1. La^{3+} is tenfold coordinated by three oxygen and seven chlorine atoms in an arrangement which can be described as a threefold (by chlorine atoms) capped trigonal ($LaO_2Cl_4Cl_3$) prism which has a third coordinating oxygen atom (distances cf. Table 6) over an edge, as shown in Fig. 2. Vanadium is tetrahedrally coordinated by four oxygen atoms ($3 \times d_{(V-O(1))} = 1.72$ Å, $d_{(V-O(2))} = 1.74$ Å). Each tetrahedron is surrounded by three La^{3+} ions so that columns of $[La_3VO_4]^{6+}$-polyhedra stacks in [001] direction are formed (Fig. 3). There are two columns shifted by $\frac{1}{2}$ along z against each other per unit cell. It should be noted, that the orientation of the $(VO_4)^{3-}$- tetrahedra of two different stacks is not fixed by symmetry. Due to the statistical distribution of vanadium atoms, the resulting tetrahedron can be aligned up or down with respect to the mirror plane perpendicular to the z-axis. The alignment of the VO_4 tetrahedra in one stack, however, is the same and coupled by stoichiometry.

Each $[La_3VO_4]^{6+}$-polyhedron is coordinated by 18 chlo-

rine atoms. Six of 12 chlorine atoms in a unit cell form *trans* face-sharing octahedra piled up in the [001] direction, thus forming empty chlorine tunnels. This structural feature, known from the UCl_3 type, has been observed for many oxochlorometallates of the rare earths (Table 1, No. 1, 3—5, as well as in the related compounds $Ln_3WO_6Cl_3$ {Ln = La–Nd, Sm–Gd} (30, 31, 32), $La_3MoO_6Cl_3$ (31), and $Ln_3UO_6Cl_3$ {Ln = La, Pr, Nd} (20)).

The coordination number of M^{5+} is reduced from C.N. = 5 (trigonal bipyramidal) to C.N. = 4 (tetrahedral) in $La_3VO_4Cl_6$ as compared to the structure of $Pr_3NbO_4Cl_6$ (6) described in the same space group $P6_3/m$. In this space group, the lowering of the coordination number of the M^{5+} and the fact that the z-value becomes a free parameter is connected. Consequently the site changes from a special to a general position. Under this circumstance, the vanadium site can only be half-occupied in $P6_3/m$. If vanadium had been placed in the special position, we would have obtained abnormally high anisotropic displacement parameters in the [001] direction.

A refinement in the subgroup $P6_3$ (No. 173) (exactly two vanadium atoms per unit cell are generated in this space group) yielded unsatisfactory results. In this case we observed residual electron density on the positions that are generated in $P6_3/m$ by a mirror plane on height

TABLE 5
La₃VO₄Cl₆: Anisotropic Displacement Parameters (Standard Deviations in Brackets)

Atom	$U(1, 1)$	$U(2, 2)$	$U(3, 3)$	$U(2, 3)$	$U(1, 3)$	$U(1, 2)$
La	0.01589(11)	0.01180(10)	0.01031(11)	0.0	0.0	0.00866(7)
V	0.00838(26)	0.00838(26)	0.01193(70)	0.0	0.0	0.00419(13)
Cl(1)	0.01332(29)	0.01460(29)	0.01645(30)	0.0	0.0	0.00771(24)
Cl(2)	0.01261(27)	0.01120(27)	0.01638(32)	0.0	0.0	0.00654(23)
O(1)	0.01018(91)	0.01081(88)	0.01466(95)	0.0	0.0	0.00349(76)
O(2)	0.0211(12)	0.0211(12)	0.0217(20)	0.0	0.0	0.01055(62)

TABLE 6
$La_3VO_4Cl_6$: Bond Distances (Å) and Angles (°) of Polyhedra about La

La	O 1	O 1	Cl 1	Cl 1	Cl 2	O 2	Cl 2	Cl 2	Cl 1	Cl 2
O 1	**2.438**	4.133	3.047	5.135	3.395	2.669	3.025	5.122	4.820	3.395
O 1	115.88	**2.438**	5.135	3.047	3.395	2.669	5.122	3.025	4.820	3.395
Cl 1	68.11	144.55	**2.950**	4.133	3.380	4.954	3.747	5.579	3.446	5.613
Cl 1	144.55	68.11	88.95	**2.950**	3.380	4.954	5.580	3.747	3.446	5.613
Cl 2	77.00	77.00	69.60	69.60	**2.973**	3.106	5.607	5.607	5.280	5.379
O 2	57.96	57.96	113.27	113.27	62.86	**2.982**	4.927	4.927	6.044	3.106
Cl 2	65.84	137.77	77.33	136.97	137.29	109.62	**3.047**	4.133	3.380	3.347
Cl 2	137.77	65.84	136.97	77.33	137.29	109.62	85.41	**3.047**	3.380	3.347
Cl 1	121.81	121.81	69.86	69.86	121.90	175.24	67.12	67.12	**3.067**	5.190
Cl 2	74.18	74.18	135.32	135.32	124.02	61.15	65.76	65.76	114.08	**3.118**

TABLE 7
$La_3VO_4Cl_6$: Bond Distances (Å) and Angles(°) of Polyhedra about V

V	O 1	O 1	O 1	O 2
O 1	**1.719**	2.926	2.926	2.669
O 1	116.67	**1.719**	2.926	2.669
O 1	116.67	116.67	**1.719**	2.669
O 2	100.64	100.64	100.64	**1.749**

$z = \frac{1}{4}$ (corresponding split positions). The residual electron density can be explained by two possibilities. Either we measured a twin (but a refinement (27) for an inverted twin in $P6_3$ gave worse results than the disorder model in $P6_3/m$) or the domains where the direction of $[(VO_4)^{3-}]_n$-polyhedra piles up is the same are very small. Thus the transition from a twin description to a statistical disordered model is fluent. Due to the better results, we prefer the structure description by the disorder model in $P6_3/m$.

ACKNOWLEDGMENTS

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