

Dedicated to Prof. Menachem Steinberg on the occasion of his 65th birthday

## TERNARY MOLYBDENUM(III) CHLORIDES

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### Abstract

The phase diagrams of  $A\text{Cl}/\text{MoCl}_3$  ( $A=\text{Na}, \text{K}, \text{Rb}, \text{Cs}$ ) were elucidated by DTA measurements in sealed quartz ampoules in the range of 0–40 mol%  $\text{MoCl}_3$ . The samples were prepared from alkali metal chlorides and the compounds  $\text{A}_3\text{MoCl}_6$  or  $\text{A}_3\text{Mo}_2\text{Cl}_9$ . The 3:1 compounds with  $A=\text{Na}, \text{Rb}, \text{Cs}$  were obtained by sintering mixtures of  $3\text{ACl}+\text{MoCl}_3$ ; the ennechlorides  $\text{A}_3\text{Mo}_2\text{Cl}_9$  with  $A=\text{K}, \text{Rb}, \text{Cs}$  were precipitated from solutions of  $\text{MoCl}_3\cdot 3\text{H}_2\text{O}$  and  $\text{ACl}$  in formic acid. Congruently melting compounds  $\text{A}_3\text{MoCl}_6$  exist in all four systems, incongruently melting ennechlorides  $\text{A}_3\text{Mo}_2\text{Cl}_9$  in systems with  $A=\text{K}, \text{Rb}, \text{Cs}$ . Still unknown structures were determined by analog-indexing powder patterns according to known structure families. Especially  $\text{Cs}_3\text{MoCl}_6$  is isotypic with the recently found  $\text{Cs}_3\text{CrCl}_6$  structure. Additionally, the unit cell parameters were determined for the compounds  $\text{A}_3\text{MoCl}_5\cdot\text{H}_2\text{O}$  ( $A=\text{K}, \text{Rb}, \text{Cs}$ ) analogous to  $\text{Cs}_2\text{TiCl}_5\cdot\text{H}_2\text{O}$ , whose structure was determined by single crystal measurements.

**Keywords:** crystal structures, phase diagrams of systems  $\text{ACl}/\text{MoCl}_3$  from 0–40 mol%  $\text{MoCl}_3$ , preparation of  $\text{A}_3\text{Mo}_2\text{Cl}_9$  from formic acid

### Introduction

Within the scope of our work on ternary chlorides in pseudobinary systems  $\text{ACl}/\text{MCl}_3$  ( $A=\text{alkali metal Na–Cs}$ ), we have investigated during the last years, in addition to lanthanide systems with  $M=\text{La–Er}$  [1] also systems with the light transition metals chromium and iron [2]. The systems with  $\text{TiCl}_3$  [3] and  $\text{VCl}_3$  [4] were already known and described in the literature. The radius of the biggest transition metal ion  $\text{Ti}^{3+}$  is 0.67 Å [5], the radius of  $\text{Er}^{3+}$  is 1.03 Å. It was now of interest for us, to extend our investigations to  $\text{Mo}^{3+}$  whose radius of 0.69 Å is between that of titanium and the smallest lanthanide ion.

A comprehensive description of the properties of  $\text{MoCl}_3$  is given by Schäfer and Schnering [6]: Red crystals, crystallising in the  $\text{AlCl}_3$ -type structure (space group  $\text{C2/m}$ ; layer structure with a cubic dense  $\text{Cl}^-$ -packing). A  $\beta$ -modification (hexagonal  $\text{Cl}^-$ -packing) is non-stoichiometric with a composition of  $\text{MoCl}_{3.08}$ . At 500°C a disproportionation begins:



It is complete after 4 h at 600°C. MoCl<sub>3</sub> is insoluble in water and hydrochloric acid. These properties have consequences for the investigation of the systems ACl/MoCl<sub>3</sub>. Areas in the phase diagrams containing free MoCl<sub>3</sub> cannot be measured at temperatures higher than 500°C, because there multi-component systems exist with at least MoCl<sub>2</sub> present. Furthermore, e.m.f.-measurements in a newly constructed H<sub>2</sub>/HCl-cell gave no constant potential. For DTA-investigations the ternary compounds A<sub>3</sub>MoCl<sub>6</sub> or A<sub>3</sub>Mo<sub>2</sub>Cl<sub>9</sub> were used, if possible. Because of the insolubility of MoCl<sub>3</sub> and its ternary Rb- and Cs-chlorides in water, no solution enthalpies could be measured.

Thus, methods for the preparation of anhydrous ternary chlorides, measurements of the phase diagrams ACl/MoCl<sub>3</sub> (A=Na–Cs) containing up to 40 mol% MoCl<sub>3</sub> and crystallographic investigations are described in this paper.

## Experimental

### *Substances*

MoCl<sub>3</sub> was prepared according to [6] by reduction of MoCl<sub>5</sub> with Mo-metal in a sealed glass tube at 500°C. The product was washed twice with anhydrous alcohol, then with anhydrous diethylether and was finally dried in vacuum at 90°C. The alkali metal chlorides (p.a. quality; Merck, Darmstadt) were dried by melting in a quartz tube in vacuum. Solutions of Mo<sup>3+</sup> were prepared by electrolytic reduction of 1 mol l<sup>-1</sup> solutions of MoO<sub>3</sub> in hydrochloric acid. The reduced solution was evaporated nearly to dryness at 20 mbar and 95°C. The dark red oil obtained was further evaporated at 0.02 mbar and 60°C for 8 h to a copper-coloured, amorphous product, foamy and extremely hygroscopic.

Analyses gave a Cl/Mo ratio of 2.81, the oxidation state of molybdenum was found to be 3.04. Thus it must be assumed that partially hydrolysed MoCl<sub>3</sub>·3H<sub>2</sub>O was formed.

MoCl<sub>5</sub> was prepared from the elements as described in Brauer [7].

Acetic acid was treated with P<sub>2</sub>O<sub>5</sub> for 4 h at boiling temperature followed by distillation at 118–119°C.

Formic acid (99–100%) was used without further treatment.

Molybdenum was determined by precipitation of molybdate with 8-hydroxyquinoline acetate [8]. Oxidation state determinations were done by cerimetric titration in sulphuric acid solutions, the titration end point was indicated potentiometrically and with ferroin.

Chloride was determined by potentiometric titration with AgNO<sub>3</sub>.

### *X-ray investigations*

Powder patterns were taken with a Philips PW 1050/25 goniometer equipped with a proportional counter and a vacuum attachment. During exposure (CuK<sub>α</sub>

radiation) the samples were under He atmosphere. The digital data were collected and analyzed with PROFIL [9]. The calculations were performed with the program LAZY PULVERIX [10]. For high-temperature photographs a Simon-Guinier camera was used. For the determination of cell parameters from powder patterns corundum ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>,  $a=475.92$  pm;  $c=1299.00$  pm) was used as internal standard. Calculations were done using the least squares method of Warczewski and de Wolff [11].

### *Differential thermal analysis (DTA)*

The DTA measurements were performed in a home built device with the samples (1 g) in vacuum-sealed quartz ampoules. If necessary, the material could be annealed after melting with a gas flame and homogenizing by shaking and quenching. In general, heating curves were measured (heating rate 2 K min<sup>-1</sup>). Calibration of temperature: *m.p.* Zn=379°C, *t.p.* K<sub>2</sub>SO<sub>4</sub>=583°C.

## **Results**

### *Preparation of ternary Mo(III)-chlorides*

From aqueous solutions

For all preparations from aqueous solutions an electrolytically reduced 1 mol l<sup>-1</sup> solution of Mo(III) in hydrochloric acid was used. After addition of aqueous solutions of ACl ( $A=K, Rb, Cs$ ) the hydrates A<sub>2</sub>MoCl<sub>5</sub>·H<sub>2</sub>O were crystallized [12]. The yield could be improved by a slight evaporation. K<sub>3</sub>MoCl<sub>6</sub> [7] was obtained by evaporation under permanent saturation with HCl (gas).

Cs<sub>3</sub>Mo<sub>2</sub>Cl<sub>9</sub> was formed according to Nyholm [13]: a MoCl<sub>3</sub>-solution was boiled down to viscous consistency and mixed with small amounts of a CsCl-solution in hot 10 mol l<sup>-1</sup> hydrochloric acid. Rb<sub>3</sub>Mo<sub>2</sub>Cl<sub>9</sub> was prepared analogously.

From anhydrous acetic acid

Dissolving MoCl<sub>5</sub> in acetic acid yields a green solution containing Mo(IV); ClCH<sub>2</sub>COOH is assumed as the oxidation product. From these solutions Cs<sub>2</sub>MoCl<sub>6</sub> and Rb<sub>2</sub>MoCl<sub>6</sub> could be precipitated by adding solutions of Cs- and Rb-acetate, respectively, in acetic acid and saturation with HCl (gas).

Attempts to reduce solutions of Mo(IV) electrolytically to Mo(III) failed because of the too low conductivity.

From anhydrous formic acid

Amorphous MoCl<sub>3</sub>·3H<sub>2</sub>O was dissolved in formic acid saturated with HCl. By adding solutions of alkali metal chlorides in formic acid, compounds A<sub>3</sub>Mo<sub>2</sub>Cl<sub>9</sub> ( $A=K, Rb, Cs$ ) precipitated. Yield: 40–70%

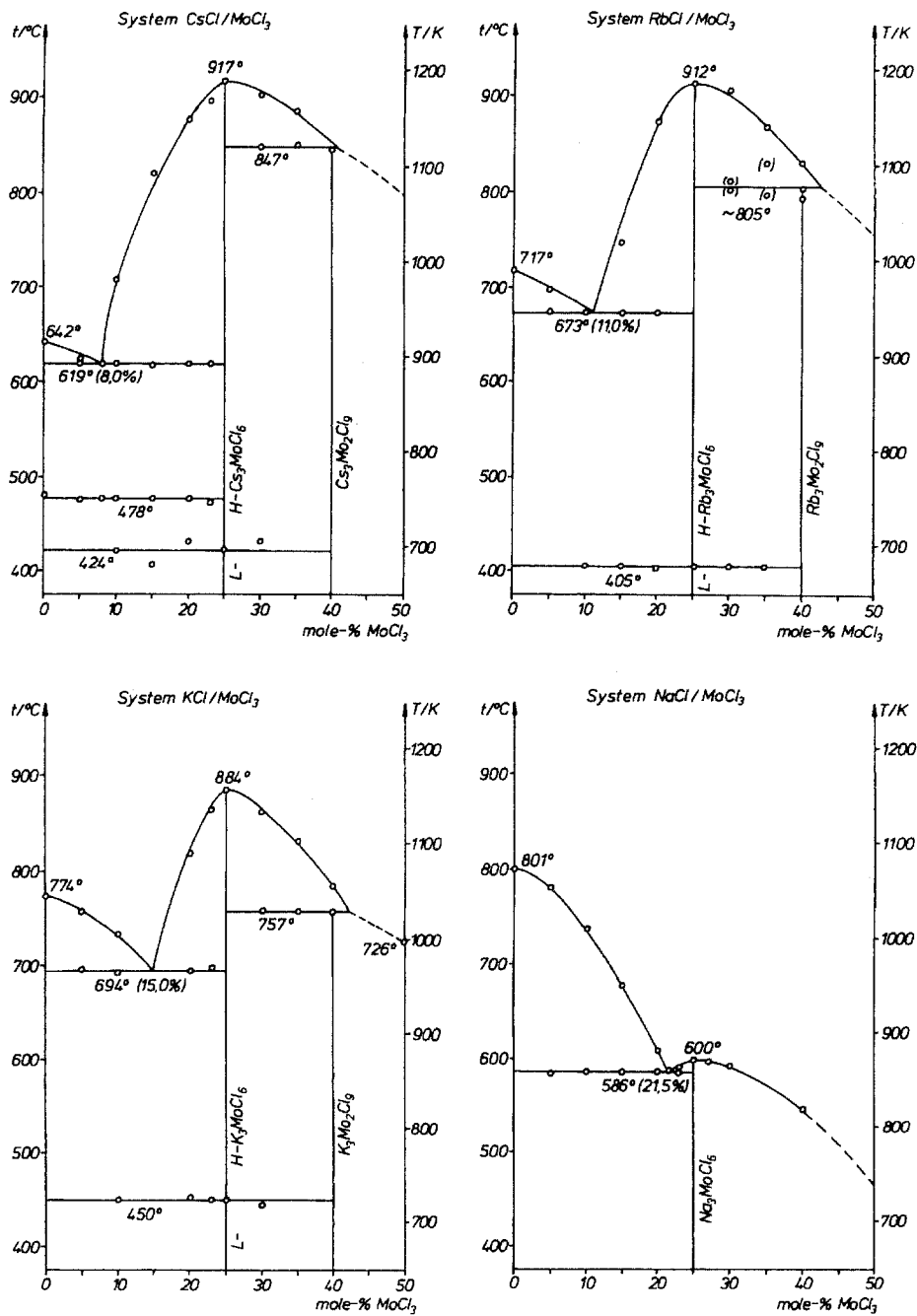


Fig. 1 Phase diagrams of the systems  $ACl/MoCl_3$  ( $A=Na, K, Rb, Cs$ )

### Preparation of $K_3Mo_2Cl_9$

0.005 mole of  $MoCl_3 \cdot 3H_2O$  were dissolved in 20 ml formic acid saturated with HCl and then the equivalent amount of solid KCl was added. This mixture was quickly brought to the boil while HCl was bubbled through. On cooling,  $K_3Mo_2Cl_9$  was crystallized. The product was washed with small amounts of the cold solvent, twice with diethylether and then dried in vacuum at  $90^\circ C$ . Brown crystals were obtained which became pink after grinding.

### Phase diagrams

Because of the decomposition of  $MoCl_3$  above  $500^\circ C$ , mentioned in the introduction, the phase diagrams could be investigated by heating and cooling curves only in the range of 0–40 mol%  $MoCl_3$ . They are shown in Fig. 1.

If available, mixtures of ACl and the ternary compounds  $A_3Mo_2Cl_9$  or  $A_3MoCl_6$  were used. The compounds  $A_3MoCl_6$  ( $A=Na, Rb, Cs$ ) were prepared by sintering pellets of  $3ACl+MoCl_3$ , all other products were obtained by precipitation. The incongruent melting points of compounds  $A_3Mo_2Cl_9$  were determined from solid samples, sealed into quartz ampoules.

The phase diagrams of the systems  $NaCl/MoCl_3$  and  $KCl/MoCl_3$  have been determined earlier: In the sodium system Ryabov *et al.* [14] found  $Na_3MoCl_6$  using  $\alpha$ - or  $\beta$ - $MoCl_3$ , with  $\beta$ - $MoCl_3$  they additionally found  $Na-MoCl_4$ . According to Ryabov *et al.* [15] the potassium system shows, besides  $K_3MoCl_6$  (congruently melting at  $873^\circ C$ ) and the incongruently melting  $K_3Mo_2Cl_9$  (peritecticum at

**Table 1** Unit cell parameters of alkali metal-chloromolybdates(III)

Compound	Spacegr.	Z	a/pm	b/pm	c/pm	$\beta/^\circ$
L- $Cs_3MoCl_6$	Pnmm	6	2317.9(5)	1131.1(2)	752.2(2)	
H- $Cs_3MoCl_6^*$	Fm3m	4	1126.6(2)			
L- $Rb_3MoCl_6$	C2/c	8	2531.8(7)	753.1(2)	1251.2(4)	100.07(5)
H- $Rb_3MoCl_6^*$	Fm3m	4	1089.6(2)			
L- $K_3MoCl_6$ [19]	P2 <sub>1</sub> /c	4	1216.0(8)	753.4(3)	1273.1(6)	108.66(1)
H- $K_3MoCl_6^*$	Fm3m	4	1062.7(1)			
$Na_3MoCl_6$	P $\bar{3}$ 1c	2	658.2(1)	658.2(1)	1221.6(2)	120
$Cs_2MoCl_5 \cdot H_2O$	Pnma	4	1437.0(4)	1019.5(2)	736.3(2)	
$Rb_2MoCl_5 \cdot H_2O$	Pnma	4	1393.9(4)	992.4(3)	720.4(2)	
$K_2MoCl_5 \cdot H_2O$	Pnma	4	1374.7(3)	973.1(2)	714.7(2)	
$Cs_2TiCl_5 \cdot H_2O$	Pnma	4	1427.3(2)	1024.2(5)	735.5(1)	
$Rb_2TiCl_5 \cdot H_2O$	Pnma	4	1374.8(5)	992.0(3)	707.1(2)	

H- $A_3MoCl_6^*$  exposures are taken at  $550^\circ C$

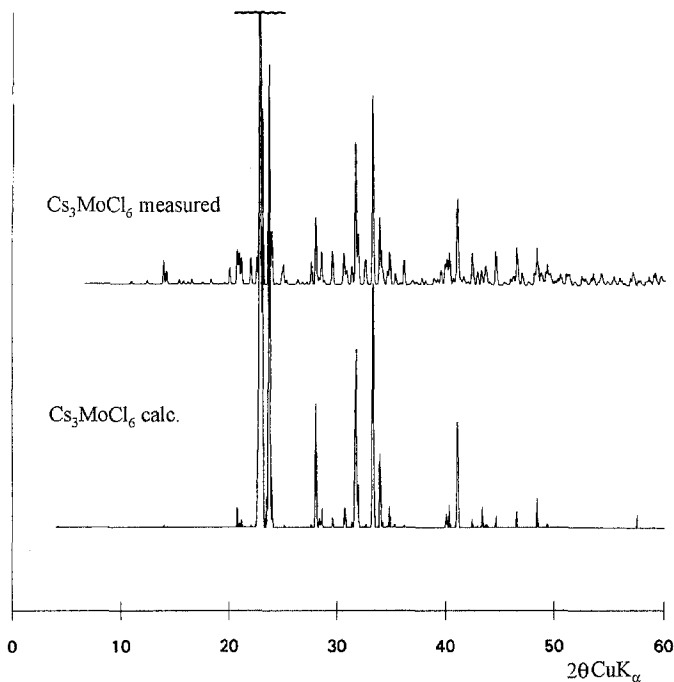


Fig. 2 Observed and calculated X-ray patterns of L- $\text{Cs}_3\text{MoCl}_6$

745°C), a compound  $\text{KMoCl}_4$  stable up to 200°C. Drobot *et al.* [16] found only the 3:1 compound  $\text{K}_3\text{MoCl}_6$  (*m.p.* = 865°C).

### X-ray investigations

The results of unit cell determinations are listed in Table 1.

Powder patterns were indexed according to the known structure families; for the intensity calculations the site parameters were taken for:

$\text{Na}_3\text{MoCl}_6$  from  $\text{Na}_3\text{CrCl}_6$  [17];  $\text{Rb}_3\text{MoCl}_6$  from  $\text{Cs}_3\text{BiCl}_6$  [18];  $\text{Cs}_3\text{MoCl}_6$  from  $\text{Cs}_3\text{CrCl}_6$  [2]; the structures of  $\text{K}_3\text{MoCl}_6$  [19] and of compounds  $\text{A}_3\text{Mo}_2\text{Cl}_9$  [20], [21] were already known. The hydrates  $\text{A}_3\text{MoCl}_5 \cdot \text{H}_2\text{O}$  were indexed analogous to  $\text{Cs}_2\text{TiCl}_5 \cdot \text{H}_2\text{O}$ ; its structure has been determined recently in our group [22] by single crystal measurements. Single crystals were obtained by slow evaporation of a solution containing  $\text{TiCl}_3$  and  $\text{CsCl}$ . The preparation of  $\text{TiCl}_3$  solutions by electrolytic reduction of  $\text{TiCl}_4/\text{HCl}$  is described in Brauer [7]. Some unpublished results are compiled in an appendix to this paper.

### Discussion

As noted in the introduction, the ionic radius of  $\text{Mo}^{3+}$  (69 pm) is somewhat larger than those of the light transition metal ions  $\text{Ti}^{3+}$ ,  $\text{V}^{3+}$ ,  $\text{Cr}^{3+}$  and  $\text{Fe}^{3+}$

(67–62 pm), but smaller than those of the later lanthanides (89 pm for  $\text{Er}^{3+}$ ). Considering the stoichiometry and the structure of the compounds –  $\text{A}_3\text{MoCl}_6$  and  $\text{A}_3\text{Mo}_2\text{Cl}_9$  – there is a close analogy with the systems of  $\text{CrCl}_3$  and  $\text{VCl}_3$  [2]: Both elements only form compounds  $\text{A}_3\text{MCl}_6$  and  $\text{A}_3\text{M}_2\text{Cl}_9$  with the same structures as found for the Mo-compounds.

The high-temperature modifications of  $\text{A}_3\text{MoCl}_6$  ( $A=\text{K, Rb, Cs}$ ) crystallize with the cubic elpasolite structure: isolated  $[\text{MoCl}_6]^{3-}$  octahedra are held together by the  $\text{A}^+$  ions; 2/3 with the CN 12 against chlorine, 1/3 in octahedral holes. The different modifications found at ambient temperature are distorted variants, in which the coordination number of the  $\text{A}^+$  ions is between 9 and 11. In  $\text{Na}_3\text{MoCl}_6$  another motif exists: here the  $\text{Na}^+$  and  $\text{Mo}^{3+}$  ions are both occupying octahedral holes.

With  $\text{Fe}^{3+}$  in tetrahedral coordination, the compounds  $\text{AFeCl}_4$  are found. Compounds  $\text{ATiCl}_4$  are also described in the literature [23]. Because of the site preference energy of the ligand field theory they are more stable than the octahedrally coordinated iron compounds such as  $\text{A}_3\text{FeCl}_6$  and  $\text{A}_3\text{Fe}_2\text{Cl}_9$ . The closest relation of molybdenum(III) is to the largest transition metal ion  $\text{Ti}^{3+}$  with  $r=67$  pm. This can be seen from the fact that  $\text{Cs}_2\text{MoCl}_5\cdot\text{H}_2\text{O}$  is isotypic with  $\text{Cs}_2\text{TiCl}_5\cdot\text{H}_2\text{O}$  (s.g. Pnma) and not with  $\text{Cs}_2\text{CrCl}_5\cdot\text{H}_2\text{O}$  (s.g. Cmcm). An explanation for the difference is given in [24]. Otherwise, the difference from the systems of the late lanthanides is significant: for instance with  $\text{Er}^{3+}$  four Cs-compounds are known:  $\text{Cs}_3\text{ErCl}_6$ ,  $\text{Cs}_2\text{ErCl}_5$ ,  $\text{Cs}_3\text{Er}_2\text{Cl}_9$  and  $\text{CsEr}_2\text{Cl}_7$  [25]. With sodium also a compound  $\text{NaErCl}_4$  exists with CN 6 for the lanthanide ion [26].

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## Appendix

Experimental data and structure refinement parameters for  $\text{Cs}_2\text{TiCl}_5\cdot\text{H}_2\text{O}$

Formula	$\text{Cs}_2\text{TiCl}_5\cdot\text{H}_2\text{O}$
Diffractometer	Enraf Nonius CAD4
Monochromator	graphite
Scanmode, width	$\Omega$ -scans/ $0.88+0.65 \tan \Theta$
Wavelength (Mo- $\text{K}\alpha$ )	71.073 pm
Crystal system	orthorhombic
Space group	Pnma
Lattice parameters (pm)	$a=1427.3(2)$
at 299 K	$b=1024.2(5)$
	$c=735.5(6)$
Volume per U.C. ( $10^6$ pm <sup>3</sup> )	1075.2(1)
Number of F.U. (Z)	4

Calculated density (g/cm <sup>3</sup> )	3.144
Absorption coefficient	8.647 mm <sup>-1</sup>
Absorption correction	empirically
min.; max. transmission	0.48; 1.00
Theta measured from	2.9–24.00
Indexing area	-16 ≤ h ≤ 0; -11 ≤ k ≤ 2; -8 ≤ l ≤ 8
Number of reflexions	2131
Symmetry independ refl.	901 [R(int)=0.0231]
R-Value (all data)	R1=0.0314, wR2=0.0686
*DIFABS, N. Wacker and D. Stuart, Acta. Cryst., A39 (1983) 158.	

Atomic positions and equivalent temperature parameters (pm) in Cs<sub>2</sub>TiCl<sub>5</sub>·H<sub>2</sub>O

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> <sub>eq</sub>
Ti	0.1097(1)	1/4	0.3176(1)	23(1)
Cl1	0.0069(1)	1/4	0.0591(2)	32(1)
Cl2	0.2414(1)	1/4	0.1097(2)	27(1)
Cl3	0.2175(1)	1/4	0.5643(2)	34(1)
Cl4	0.1012(1)	0.0113(1)	0.3291(2)	32(1)
O	-0.0055(3)	1/4	0.4995(7)	41(1)
Cs	0.3552(1)	-0.0011(1)	0.3436(1)	32(1)
H	-0.0267(39)	0.3162(63)	0.5125(76)	74(23)

(Selected)	Angular <sup>o</sup> and internuclear distances (pm)		
O–TiCl1	91.5(2)	Ti–O	212.5(5)
O–Ti–Cl2	180.0(2)	Ti–Cl1	240.2(2)
O–Ti–Cl4	86.54(4)	Ti–Cl2	242.3(2)
Cl1–Ti–Cl2	88.54(6)	Ti–Cl3	237.9(2)
Cl1–Ti–Cl4	89.84(4)	Ti–Cl4	244.95(10)
Cl2–Ti–Cl3	88.83(6)		
Cl2–Ti–Cl4	93.46(4)		
Cl3–Ti–Cl4	90.32(3)		

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