THERMOCHEMICAL AND STRUCTURAL INVESTIGATIONS ON ALKALI METAL CHLORIDES-IRON(III)-CHLORIDE SYSTEMS

M. Prien and H. J. Seifert

Inorganic Chemistry, University GH Kassel, 03500 Kassel, Germany

Abstract

The pseudobinary systems $ACl-FeCl_3$ ($A = $Na, K, Rb, Cs) were reinvestigated by means of differential thermal analysis and X-ray powder diffraction. The existence of the compounds $AFeCl_4$ ($A = $Na–Cs) and $Cs_3Fe_2Cl_9$ could be confirmed; $Cs_3Fe_2Cl_9$ is a stable compound which decomposes to CsCl and $CsFeCl_4$ above 270°C. Additionally, two Rb-compounds – Rb_3FeCl_6 and $Rb_3Fe_2Cl_9$ – were found, which decompose, when heated, in the solid state. $Rb_3Fe_2Cl_9$ is isotypic with the analogous Cs-compound; Rb_3FeCl_6 has the Cs_3BiCl_6 structure. Cs_3FeCl_6 is isotypic with Cs_3CrCl_6, a recently found orthorhombic variant of the elpasolite type.

Keywords: DTA, pseudobinary systems $ACl-FeCl_3$, solution calorimetry, XRD

Introduction

Investigations of phase diagrams of the systems $ACl-FeCl_3$ ($A = $Cs, Rb, K, Na) have provided differing results. Early investigations by Johnstone [1] and Morozow [2] describe the systems $NaCl-FeCl_3$ and $KCl-FeCl_3$ as purely eutectic, whereas Cook [3] found compounds $NaFeCl_4$ and $KFeCl_4$. According to Morozow [4] such a 1:1-compound also exists in the systems with RbCl and CsCl. Later Kovsarnechan [5] and Feist [6] found a compound $Cs_3Fe_2Cl_9$ in the system $CsCl-FeCl_3$, which decomposes in the solid state. They gave differing descriptions about a further compound Cs_3FeCl_6. According to Kovsarnechan it melts incongruently at 480°C and undergoes a polymorphic phase transition at 345°C, whereas Feist describes the compound as metastable at all temperatures. – The crystal structures of all compounds $AFeCl_4$ are well known from the work of Meyer [7]; they all contain $[FeCl_4]^-$ – tetrahedra. The enneachloride $Cs_3Fe_2Cl_9$ crystallizes in the hexagonal space group $P6_3/mmc$ [5].

In this paper all systems were studied by DTA and XRD measurements. Of special interest were two questions:

1) Does a stable compound Cs_3FeCl_6 exist?

2) Are there more compounds other than RbFeCl$_4$ in the system RbCl–FeCl$_3$?

Furthermore, formation enthalpies for the formation of some chloro-ferrates(III) from ACl and FeCl$_3$ at ambient temperature were determined, and previously unknown crystal structures were investigated by analogous indexing of powder patterns.

Experimental

Source of primary compounds

FeCl$_3$ (Fa. Merck, quality pa.) was purified by sublimation in a Cl$_2$-stream (*mp.* = 318°C). The alkali metal chlorides were dried by heating at 500°C.

Differential thermal analysis

The laboratory-built DTA device has already been described [8]. Mixtures of ACl and FeCl$_3$ (~0.5 g, prepared in a glove-box) were melted in sealed quartz ampoules in a gas flame, then quenched and, if necessary, annealed. With these samples heating curves (2 deg·min^{-1}) were measured, followed by cooling curves.

X-ray diffraction

Powder patterns at ambient temperature were taken with a Philips PW 1050/25 goniometer equipped with a proportional counter and a vacuum attachment. During exposure (CuK$_\alpha$-radiation) the samples were under He atmosphere. Al$_2$O$_3$ (a=475.92 pm; τ=1299.00 pm) was used as internal standard for the calculation of unit cell parameters (LAZY PULVERIX [9]).

Solution calorimetry

The apparatus used was a laboratory-built isoperibolic calorimeter [10] with a volume of 1.3 l. Samples of 3–6 g thus yielded virtually ideal solutions (dissolution ratio 1:3500 mol/mol). Each ΔH was measured at least in triplicate. The alkali chlorides were dissolved in a solution of LaCl$_3$ of adequate concentration.

Results

Phase diagrams

The phase diagrams of the systems CsCl–FeCl$_3$ and RbCl–FeCl$_3$, which are different from literature data, are given in Fig. 1.

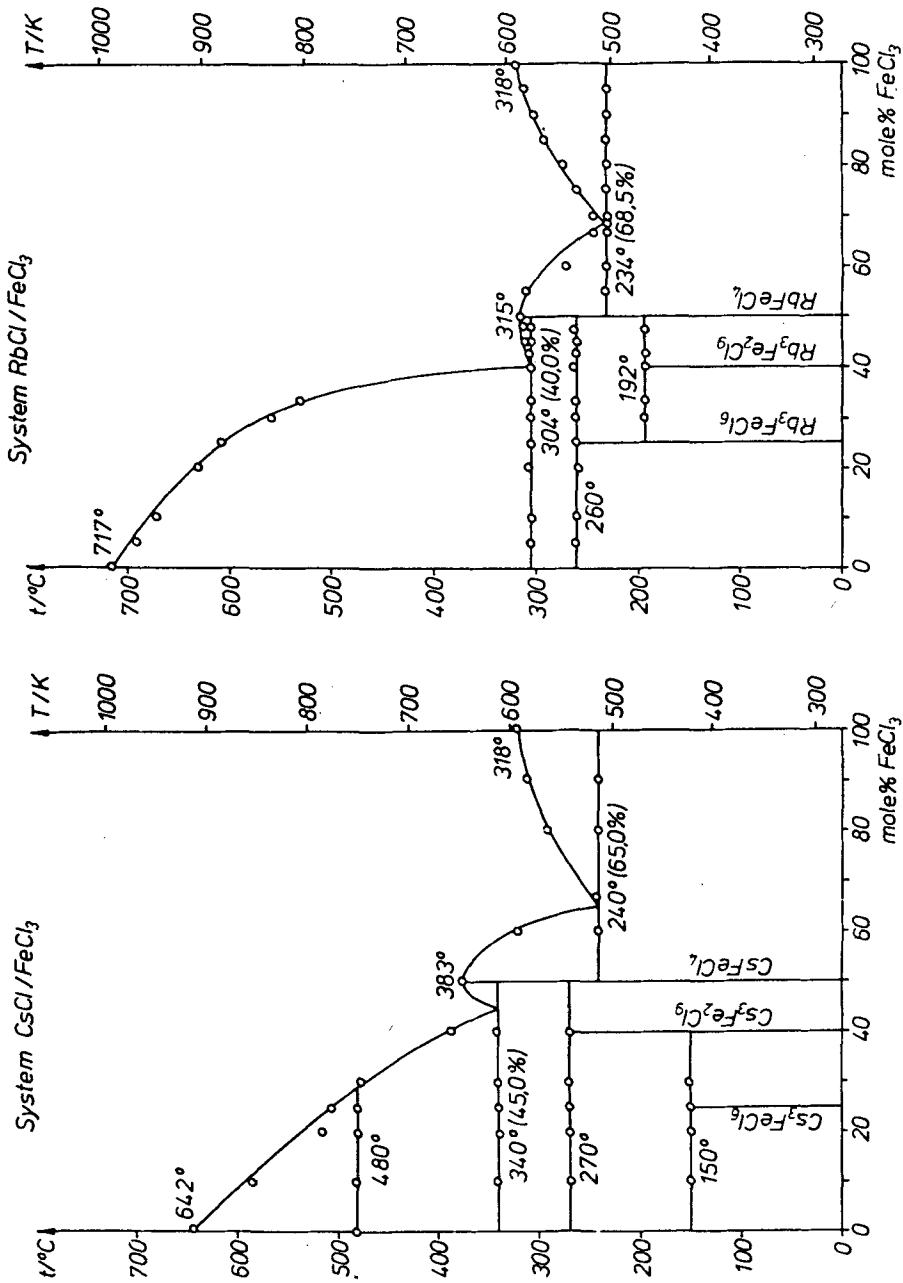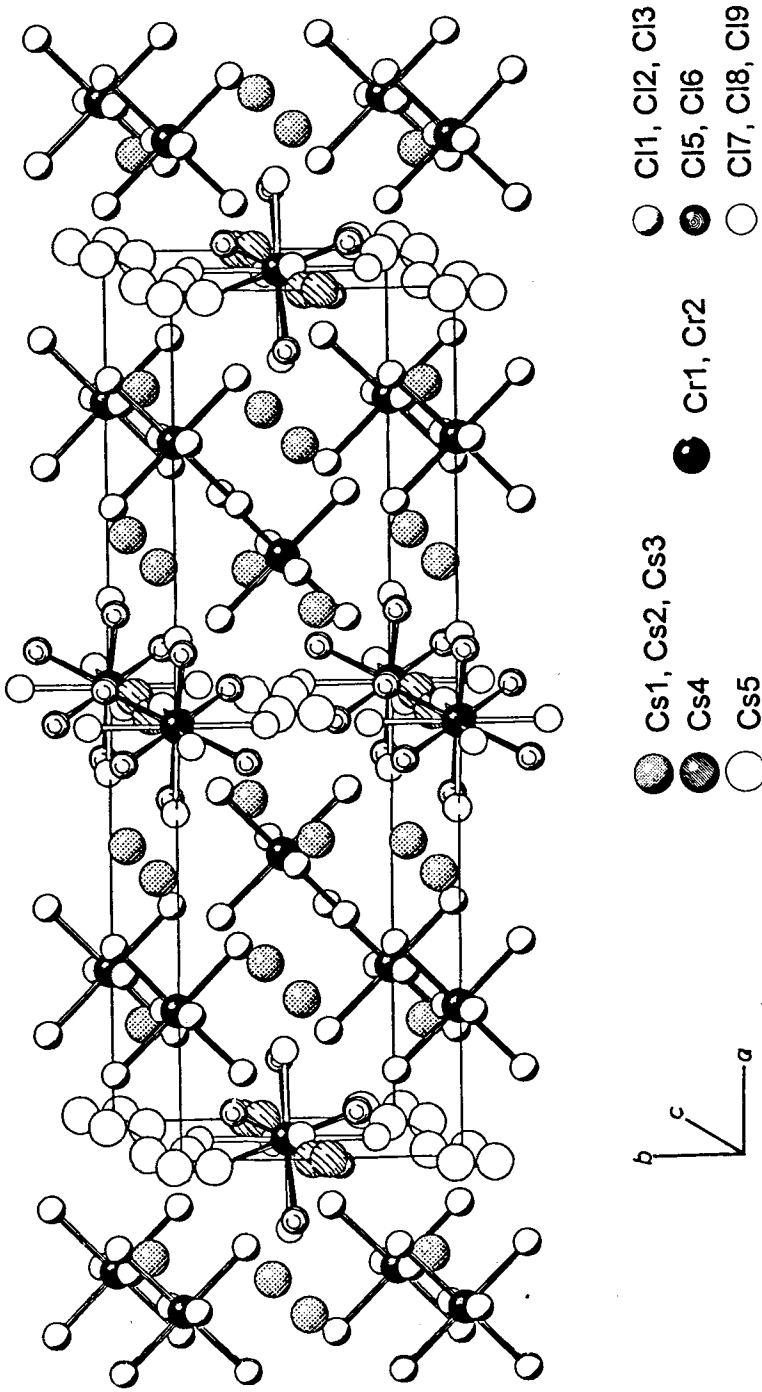**Fig. 1** Phase diagrams of the systems CsCl– FeCl₃ and RbCl– FeCl₃

Fig. 2 Unit cell of Cs_3CrCl_6

System CsCl–FeCl₃

Beside the congruently-melting compound $CsFeCl_4$ two other chloroferrates exist, which decompose in the solid state. The decomposition of $Cs_3Fe_2Cl_9$ is well reversible in the timescale of DTA. The thermal effect was found at 270°C in heating curves and at ~240°C in cooling curves. The decomposition temperature of Cs_3FeCl_6 was found in heating curves at 150°C; the reverse reaction during cooling is so slow that it could not be detected. Therefore, we had to prepare pure Cs_3FeCl_6 by dehydration of $Cs_3FeCl_6 \cdot H_2O$ in a HCl-stream at 120°C. The hydrate was synthesized in acetic acid as solvent, as recently described [11].

Kovsarnechan [5] found two thermal effects for a sample with 25 mole % $FeCl_3$. However, the effect at 345°C must be attributed to the eutectic at 45.5 mole % $FeCl_3$, the effect at 481°C to the α–β-transition of CsCl.

The system RbCl–FeCl₃

The results of Morozow [4] – existence of a congruently melting compound $RbFeCl_4$ and two eutectics – could be confirmed. Additionally two other compounds were found; $Rb_3Fe_2Cl_9$ decomposes in the solid state at 192°C and Rb_3FeCl_6 at 260°C. It must be pointed out that the formation of these two compounds from quenched melts of the adequate composition occurred only by annealing the sample for ~4 weeks at temperatures higher than ~140°C. When they were heated above their decomposition temperatures and then annealed, their X-ray patterns displayed the peaks $RbCl + RbFeCl_4$ or $Rb_3FeCl_6 + RbFeCl_4$, respectively.

Systems KCl–FeCl₃ and NaCl–FeCl₃

According to Cook [3] the compounds $AFeCl_4$ exist in both systems. We could confirm these findings and found melting temperatures of 252°C for $KFeCl_4$ and 163°C for $NaFeCl_4$. A polymorphic transition for $KFeCl_4$ occurs at 154°C.

Crystal structures

Until now the structures of the 3:1-compounds and of $Rb_3Fe_2Cl_9$ were unknown. The unit cell parameters are compiled in Table 1.

For the intensity calculations for the two Rb-compounds the site parameters of the ions were taken from $Cs_3Fe_2Cl_9$ [5] and Cs_3BiCl_6 [12], respectively.

Cs_3FeCl_6 is isotypic with Cs_3CrCl_6 whose structure was solved recently in our group (still unpublished). It is a hitherto unknown distortion variant of the epasolite type. In the orthorhombic space group Pnnm six formula units exist. In Table 2 the results of an intensity calculation for the first 20 observed reflec-

tions are compiled. (It must be pointed out that there is a disorder of some Cs^+-
and Cl^--ions, given by an occupation factor 0.5.)

Table 1 Unit cell parameters of hitherto unknown chloroferrates(III) with cesium and rubidium

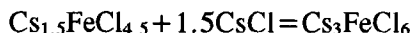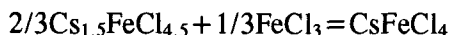| Compounds	Stucture type	a/pm	b/pm	c/pm	β / °
Cs_3FeCl_6	Cs_3CrCl_6–Pnnm	2306.0(6)	1120.8(2)	749.7(2)	
Rb_3FeCl_6	Cs_3BiCl_6–C2/c	2501.5(2)	760.0(2)	1233.6(7)	100.7°
$Rb_3Fe_2Cl_9$	$K_3W_2Cl_9$–P6₃/mmc	704.9(8)		1757.8(4)	

Solution calorimetry

Cook *et al.* [3] found by solution calorimetry that the compounds $NaFeCl_4$
and $KFeCl_4$ are formed from ACl and $FeCl_3$ in exothermic reactions. We have
measured such enthalpies for all those compounds which could be prepared in
stoichiometrically pure form (Table 2). To avoid hydrolysis, the compounds
were dissolved in 0.1 m hydrochloric acid. For the binary compounds the fol-

Table 2 Crystal data for Cs_3FeCl_6 in S.G. Pnnm (CuKα–radiation)

hkl	$v_{calc.}$	$I_{calc.}$	$v_{exp.}$	$I_{exp.}$
311	9.20	1	9.16	1
121	10.08	4	10.08	6
510	10.41	7	10.35	7
411	10.50	7	10.46	10
221	10.62	5	10.60	5
420	11.06	6	11.09	5
501	11.32	7	11.32	7
321	11.47	100	11.49	100
600	11.57	33	11.52	35
002	11.87	42	11.88	45
511	12.00	2	12.07	14
130	12.07	11		
230	12.53	3	12.56	7
427	12.57	4		
312	13.82	4	13.85	9
231	13.89	4		
620	14.08	23	14.10	30
022	14.33	13	14.31	15
701	14.81	6	14.84	11
222	14.85	4		

lowing $\Delta_{sol}H^{\circ}_{298}$ values were found: $FeCl_3 = -142.5$, $NaCl = +4.1$, $KCl = +17.6$; $RbCl = +17.3$; $CsCl = 17.6 \ kJ \cdot mol^{-1}$.

The synproportionation reactions for the Cs-compounds are:

$$2/3Cs_{1.5}FeCl_{4.5} + 1/3FeCl_3 = CsFeCl_4$$

$$1/4Cs_3FeCl_6 + 3/4CsFeCl_4 = Cs_{1.5}FeCl_{4.5}$$

$$Cs_{1.5}FeCl_{4.5} + 1.5CsCl = Cs_3FeCl_6$$

Table 3 Solution enthalpies and derived values in $kJ \cdot mol^{-1}$ for chloroferrates(III)

Compound	$\Delta_{sol}H^{\circ}$	$\Delta_f H^{\circ}$	$\Delta_{syn}H^{\circ}$
NaFeCl₄	–131.4	–7.0	–
KFeCl₄	–91.0	–33.9	–
RbFeCl₄	–75.3	–49.9	–
CsFeCl₄	–68.0	–56.9	–3.6
1/2Cs₃Fe₂Cl₉	–36.2	–79.9	–19.0
Cs₃FeCl₆	–10.3	–79.4	0.5

$\Delta_{sol}H^{\circ}$ = solution enthalpy; $\Delta_f H^{\circ}$ = enthalpy of formation from the binary compounds; $\Delta_{syn}H^{\circ}$ = synproportionation enthalpy

Discussion

The ionic radii (Shannon [13]) of Cr^{3+} (0.62 Å) and Fe^{3+} (0.65 Å) differ only slightly. Thus, both trichlorides form layer structures with $MCl_{6/2}$-octahedra. However, $CrCl_3$ has a melting point of 1150°C, $FeCl_3$ of 318°C. Consequently, the melting points of the compounds A_3CrCl_6 and $A_3Cr_2Cl_9$ lie higher than 800°C, while the analogous Cs- and Rb-compounds of Fe(III) decompose near 200°C.

But there is still a second reason for the low temperature of stability. The dominating compounds in the $FeCl_3$-systems are the tetrachloroferrates $AFeCl_4$ with isolated $FeCl_4$-tetrahedra [7]. They melt congruently at temperatures in the range of 160–390°C. This can be explained by the site–preference–energy (SPE) of the ligand field theory, which requires for Cr^{3+} a SPE $1/2 \ \Delta_{oct}$ for an octahedral environment and for Fe^{3+} $1/2 \ \Delta_{oct}$ for coordination tetrahedra.

The electron configuration of the d^3-system of Cr^{3+} is t_{2g}^3 for octahedra with non-bonding t_{2g}-orbitals and $e_g^2 \ t_{2g}^{*1}$ for tetrahedra with anti-bonding t_{2g}^*-orbitals. Thus, a destabilisation of Δ_{tetr} (ligand-field splitting in tetrahedra) or – with $\Delta_{tetr} \sim 1/2\Delta_{oct}$ – of $1/2\Delta_{oct}$ exists for the tetrahedral coordination. For the $3d^5$-system of Fe^{3+} the configuration in octahedral coordination is $t_{2g}^3 \ e_g^{*2}$ which gives a destabilisation of $2\Delta_{oct}$. For tetrahedral surroundings the configuration is $e_g \ t_{2g}^{*3}$ with a destabilisation $3\Delta_{tetr} \sim 1^{1/2}\Delta_{oct}$. Thus a SPE of $1/2\Delta_{oct}$ exists for tetrahedra.

The other two elements which form sufficiently stable chloro-metallates(III) are Ti(r_{Ti}^{3+}=0.67 Å) and V(r_V^{3+}=0.64). However, descriptions of phase diagrams ACl/MCl$_3$ were inconsistent. For titanium the existence of compounds A$_3$TiCl$_6$ and A$_3$Ti$_2$Cl$_9$ were proved by X-ray results; additionally 1:1-compounds ATiCl$_4$ were said to exist [14]. In the VCl$_3$-systems only the compounds with octahedral coordination were proved [15].

<p align="center">* * *</p>

Appendix

Experimental data and structure refinement paramerters for Cs$_3$CrCl$_6$

Formula	Cs$_3$CrCl$_6$
Crystal system	orthorombic
Space group	Pnnm (No. 58)
Lattice parameters (pm)	a =2294.7 (7)
determined at 298 K with	b =1117.5 (3)
25 reflections	c =744.6 (2)
Volume (10^6 pm^3)	1909.4 (8)
Number of F.U.	6
Calculated density (g/cm^3)	3.462
Scan-width (ω-scan)	1.0°±0.70 (tanΘ)°
Collected reflections	2863 (2.5 < Θ < 24)
within	0≤h≤14
	–7≤k≤12
	–20≤l≤2
Independent reflections with F_o > 0	1477
Agreement factors of equivalent reflections (R_{int})	0.0357
Absorption coefficient μ (mm^{-1})	8.50
Absorption correction	semi-empirical (ψ-scans)
Number of refined parameters	106
Reliability factors[a]	R=0.0357 for F_o < 4σ
	wR_2 = 0.0933 for all data
	GooF = 1.113

[a] Definitions of reliability factors: $R = \Sigma\ ||F_o|-|F_c||\ /\Sigma\ |F_o|$
$$wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$$

Atomic coordinates and equivalent temperature parameters (pm^2) in Cs_3CrCl_6

Atom	x/a	y/b	z/c	U_{eq}
4 Cs1 in g	0.13316	0.47603	0.00000	0.04029
4 Cs2 in g	0.18820	0.20109	0.50000	0.04974
4 Cs3 in g	0.32767	0.24408	0.00000	0.04905
4·0.5 Cs4 in g	0.49416	0.62127	0.00000	0.03469
8·0.5 Cs5 in h	0.00185	0.19739	0.06997	0.04184
4 Cr1 in g	0.32784	0.48011	0.50000	0.02367
2 Cr2 in d	0.00000	0.50000	0.50000	0.02568
8 Cl1 in h	0.25513	0.47012	0.27809	0.04030
4 Cl2 in g	0.32412	0.68980	0.50000	0.04500
8 Cl3 in h	0.40021	0.48957	0.27402	0.04340
4 Cl4 in g	0.33687	0.26991	0.50000	0.04237
8·0.5 Cl5 in h	0.03693	0.62945	0.27874	0.05125
4·0.5 Cl6 in g	0.08823	0.39468	−0.50000	0.07192
4·0.5 Cl7 in f	0.00000	0.50000	0.18394	0.03494
4·0.5 Cl8 in g	0.01370	0.71079	−0.50000	0.04565
4·0.5 Cl9 in g	0.10111	0.47022	−0.50000	0.04645

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Zusammensetzung — Die Zustandsdiagramme der pseudobinären Systeme ACl–FeCl₃ (A = Na, K, Rb, Cs) wurden mittels Differenzthermoanalyse und Röntgenbeugung an Kristallpulvern neu untersucht. Die Existenz der bekannten Verbindungen AFeCl₄ (A = Na–Cs) und Cs₃Fe₂Cl₉ wurde bestätigt; Cs₃Fe₂Cl₉ ist eine stabile Verbindung, die oberhalb 270°C zu CsCl und CsFeCl₄

zerfällt. Neu gefunden wurden die Verbindungen $Rb_3Fe_2Cl_9$ und Rb_3FeCl_6, die beide beim Erhitzen im festen Zustand zerfallen. Das Enneachlorid ist isotyp mit $Cs_3Fe_2Cl_9$, die 3:1-Verbindungen kristallisiert im Cs_3BiCl_6-Typ. Cs_3FeCl_6 ist isotyp mit Cs_3CrCl_6, das in einer neugefundenen orthorhombischen Verzerrungsvariante des Elpasolith-Typs kristallisiert.