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COMPOUNDS IN THE BINARY PHASE DIAGRAMS OF
THE MONOVALENT CHLORIDES WITH THE
MULTIVALENT CHLORIDES

by

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INTRODUCTION

The phase-diagram literature was surveyed to the end of 1960. Information about the binary systems of monovalent with multivalent chlorides was observed. Compounds of double chlorides occurring in these systems are listed in tabular form together with the available structural information.

A key to the abbreviations used in these tables is to be found on page 12.

Valency of Central Ion	Compound	Melting Pt., °C	Crystal Data			Preparation	Literature			Remarks
			Complete or Incomplete	Crystal Class	Space Group		Phase Diagram	Crystal Structure	Preparation	
I	Cs ₂ LiCl ₃	I 380					192			
	Rb ₂ CuCl ₃	I 250					100			
	K ₂ CuCl ₃	I 245	Co	Orth	Pnam	aq	101	3	3	
	Tl ₂ CuCl ₃	I 225					201			
	Cs ₂ AgCl ₃		Co	Orth	Pnam	aq		3	3	
	Tl ₂ AgCl ₃	I 252					202			
	Cs ₃ Cu ₂ Cl ₅	I 320					102			
	Tl ₃ Ag ₂ Cl ₅	I 252					203			
	CsLiCl ₂	I 351					192			
	RbLiCl ₂	I 321					103			
	KCuCl ₂					aq			157	
	CsAgCl ₂	I 310					104			
	N(CH ₃) ₄ ICl ₂		Co	Tet	P4 ₂ 1m	aq		2	2	
	Rb ₂ Cu ₃ Cl ₅	I 290					100			
	(NH ₄) ₂ Cu ₃ Cl ₅					aq			157	
	CsCu ₂ Cl ₃	C 274	Co	Orth	Cmcm	aq	102	1	1	
II	K ₄ MnCl ₆	I 444					105			
	Na ₄ MnCl ₆	C 496	Co	Hex	R ₃ c	aq	105	41	41	
	K ₃ NaFeCl ₆		Co	Hex	R ₃ c	aq		42	42	Occurs as mineral
	Li ₄ CoCl ₆	I 475					5	43	43	
	(NH ₄) ₄ ZnCl ₆	C 340		(Hex)		aq	107	44	44	(Hex) = crystal habitus
	K ₄ PdCl ₆					aq			184	
	Rb ₄ CdCl ₆		In	Hex	R ₃ c	aq		46	46	
	K ₄ CdCl ₆	I 461	Co	Hex	R ₃ c	aq	108	45 46	46	
	(NH ₄) ₄ CdCl ₆	C 340	In	Hex	R ₃ c	aq	107	47	47	
	Tl ₄ HgCl ₆	I 250						46	46	
	(NH ₄) ₄ HgCl ₆	I 243				PD	109	48	48	
	Cs ₄ PbCl ₆					aq		49	49	
								50	177	
	K ₄ PbCl ₆	I 480					106			
	Cs ₃ MgCl ₅	C 527					117	50		
	Cs ₃ MnCl ₅	C 511					112			
	(N ₂ H ₅) ₃ MnCl ₅	240				aq			158	
	Cs ₃ CoCl ₅	C 549	Co	Tet	I ₄ /mcm	aq	5	39	39	
	Rb ₃ CoCl ₅	I 510	In	Tet	I ₄ /mcm	aq	5	39	39	
	Cs ₃ ZnCl ₅	I 560					118			
	Tl ₃ ZnCl ₅	C 344					205			
	(NH ₄) ₃ ZnCl ₅	C 340	Co	Orth	Pmna	aq, PD	107	40	40	
	Rb ₃ CdCl ₅	I 471					119			
	Tl ₃ SnCl ₅	C 310					199			
	Cs ₃ HgCl ₅					aq			176	
	Tl ₃ PbCl ₅	C 397					198			
	Cs ₅ Co ₂ Cl ₉	I* 475					5			I* 475, compd decomposes in solid state
	Na ₂ BeCl ₄	I 310					120			
	Li ₂ BeCl ₄	I 350					120			

Valency of Central Ion	Compound	Melting Pt., °C	Crystal Data			Preparation	Literature			Remarks
			Complete or Incomplete	Crystal Class	Space Group		Phase Diagram	Crystal Structure	Preparation	
II	Tl ₂ BeCl ₄	C 458					120			
	Cs ₂ MgCl ₄	C 545					117			
	Rb ₂ MgCl ₄	C 480					121			
	K ₂ MgCl ₄	C 443					122			
	Na ₂ MgCl ₄	I 485					123			
	K ₂ TiCl ₄	I 675					134			
	Na ₂ TiCl ₄	I* 548					110			I* 548, compd. decomposes in solid state
	K ₂ VCl ₄	I* 650					111			I* 650, compd. decomposes in solid state
	Cs ₂ MnCl ₄	C 538					112			
	Rb ₂ MnCl ₄	I 462					112			
	(Ph ₃ MeAs) ₂ MnCl ₄					Et OH			171	
	Cs ₂ FeCl ₄	C 566					113			
	K ₂ FeCl ₄	I 380					114			
	(NH ₄) ₂ FeCl ₄					aq			160	
	(Ph ₃ MeAs) ₂ FeCl ₄					Et OH			171	
	Cs ₂ CoCl ₄	C 597	Co	Orth	Pnma	aq	5	25 26	25 26	
	Rb ₂ CoCl ₄	C 538	In	Orth	Pnma	PD	5	5	5	α form
	K ₂ CoCl ₄	C 436					5			
	Na ₂ CoCl ₄	I* 370					124			I* 370, compd. decomposes in solid state
	Li ₂ CoCl ₄	I* 370					5			I* 370, compd. decomposes in solid state
	(NMe ₄) ₂ CoCl ₄		In	Orth	Pnam	aq		27 28	27 28	
	(Ph ₃ MeAs) ₂ CoCl ₄					Et OH			171	
	Cs ₂ NiCl ₄							26		Quadratic coordination?
	Rb ₂ NiCl ₄					aq			183	Mag. susc. ⁽⁹⁾
	(Ph ₃ MeAs) ₂ NiCl ₄					Et OH			171	
	Cs ₂ CuCl ₄	472*	Co	Orth	Pnam	aq		30,29 27	30,29 27	Spectra of crystal and solutions 472* separate determination of mp
	K ₂ CuCl ₄	C 330					101			
	(NMe ₄) ₂ CuCl ₄		In	Orth	Pnam	aq		27,30 31	27,30 31	
	(Ph ₃ MeAs) ₂ CuCl ₄					Et OH			171	
	Cs ₂ ZnCl ₄	C 601	Co	Orth	Pnam	aq	118	32	32	
	Rb ₂ ZnCl ₄	C 528					118			
	K ₂ ZnCl ₄	C 446	In	Orth	Pbm2	aq	125	33	33	
	Na ₂ ZnCl ₄	I 410					126			
	Na ₂ ZnCl ₄ ·3H ₂ O		Co	Hex	P3 ¹ m	aq		34	34	
	Li ₂ ZnCl ₄	I 354					127			
	Tl ₂ ZnCl ₄	C 360					205			
	(NH ₄) ₂ ZnCl ₄	C 340					107			
	(NMe ₄) ₂ ZnCl ₄		Co	Orth	Pnam	aq		27,28	27,28	
	(N ₂ H ₅) ₂ ZnCl ₄					aq			172	
	(Ph ₃ MeAs) ₂ ZnCl ₄					Et OH			171	
	K ₂ SrCl ₄	C 597					128			
	(NH ₄) ₂ SrCl ₄		Co	Cub	I 43			35		
	Cs ₂ CdCl ₄	C 462					116			
	Rb ₂ CdCl ₄	C 440					116			
	Na ₂ CdCl ₄	I 426					108			
	(N ₂ H ₅) ₂ CdCl ₄					aq			172	
	Cs ₂ PdCl ₄					aq			184	
	Rb ₂ PdCl ₄					aq			184	
	K ₂ PdCl ₄		Co	Tet	P4 ² m P4/mmm	aq		36,37	36,37	
	(NH ₄) ₂ PdCl ₄		Co	Tet	P4/mmm	aq		36	36	

Valency of Central Ion	Compound	Melting Pt., °C	Crystal Data			Preparation	Literature			Remarks
			Complete or Incomplete	Crystal Class	Space Group		Phase Diagram	Crystal Structure	Preparation	
II	Rb ₂ SnCl ₄	I 262					129			
	(N ₂ H ₅) ₂ SnCl ₄					aq			173	
	Rb ₂ BaCl ₄	C 670					119			
	K ₂ BaCl ₄	C 654					130			
	Cs ₂ PtCl ₄					aq			194	
	Rb ₂ PtCl ₄					aq			194	
	K ₂ PtCl ₄		Co	Tet	P4/mmm	aq		38	38	
	(NH ₄) ₂ PtCl ₄					aq			194	
	Cs ₂ HgCl ₄					aq			176	
	Rb ₂ HgCl ₄					aq, HCl			176	
	K ₂ HgCl ₄	I 245				aq	109		176	
	Na ₂ HgCl ₄					aq			193	
	(NH ₄) ₂ HgCl ₄	I 210					109			
	(N ₂ H ₅) ₂ HgCl ₄					aq			174	
	Cs ₂ PbCl ₄					aq			177	
	Rb ₂ PbCl ₄	I 448					131			
	K ₂ PbCl ₄	I 490					125			
	(NH ₄) ₂ PbCl ₄					special aqua.			177	Stable above 70°C, crystallize from hot H ₂ O
	Rb ₃ Mn ₂ Cl ₇	I 475					112			
	Cs ₃ Co ₂ Cl ₇	I* 444					5			I* 444, compd. decomposes in solid state
	K ₃ Zn ₂ Cl ₇	I* 250					125			
	TlBeCl ₃	C 368					120			
	CsMgCl ₃	C 610	In	Hex		PD	117	5		Isotype CsNiCl ₃
	RbMgCl ₃	C 542					121			
	KMgCl ₃	C 492					122			
	NaMgCl ₃	I 465					123			
	CsCaCl ₃	C 910					132			
	RbCaCl ₃	C 855					132			
	KCaCl ₃	C 745					133			
	TlCaCl ₃	I 683					199			
	KTlCl ₃	C 775					134			
	NaTiCl ₃	I 628					110			
	CsVCl ₃	C 1090	In	Hex		PD	111	6	6	Isotype CsNiCl ₃
	KVCl ₃	C 930	In	Hex		PD	111	6	6	Isotype CsNiCl ₃
	CsMnCl ₃	C 593					112			
	RbMnCl ₃	C 552					112			
	KMnCl ₃	C 496					105			
	TiMnCl ₃	I 497					204			
	(PyH) ⁺ MnCl ₃					aq			159	
	CsFeCl ₃	C 558					113			
	KFeCl ₃	C 339					114			
	CsCoCl ₃	C 547	In	Hex		PD	5	5	5	Isotype CsNiCl ₃
	RbCoCl ₃	C 485	In	Hex		PD	5	5	5	Isotype CsNiCl ₃
	KCoCl ₃	I 360	In	Hex		PD	5	5	5	Isotype CsNiCl ₃
	LiCoCl ₃	I* 270					5	5	5	I* 270, compd. decomposes in solid state
	CsNiCl ₃	730*	Co	Hex	Cmmc	aq		7	8	730* separate determination of mp
	RbNiCl ₃					conc. HCl			9	
	NH ₄ NiCl ₃					aq			8	
	MeNH ₃ NiCl ₃					Et OH			8	

Mag. Susc.⁽⁹⁾ two unpaired electrons Kz = 6

Valency of Central Ion	Compound	Melting Pt., °C	Crystal Data			Preparation	Literature			Remarks
			Complete or Incomplete	Crystal Class	Space Group		Phase Diagram	Crystal Structure	Preparation	
II	Me ₂ NH ₂ NiCl ₃					Et OH			8	
	(Me ₃ NH)NiCl ₃					Et OH			8	
	(Me ₄ N)NiCl ₃					Et OH			8	
	PrNH ₃ NiCl ₃					acid		8	8	
	BuNH ₃ NiCl ₃					Et OH		8	8	
	CsCuCl ₃	441*	Co	Hex	P6 ₁ 2	aq		10 11	10 11	441* mp separately determined
	KCuCl ₃	C 364	Co	Mon	P2 ₁ /c	from HAc	101	12	12	
	(N ₂ H ₅)ZnCl ₃					aq			172	
	CsSrCl ₃	C 907					115			
	RbSrCl ₃	C 705					115			
	TiSrCl ₃	I 569					199			
	CsCdCl ₃	C 545	Co	Mon	P2 ₁ /m	aq	116	13	13	
	RbCdCl ₃	C 466	Co	Cub	Pm3m?	aq	119	14,15	14,15	
	KCdCl ₃	C 431	Co	Orth	Pnma	aq	119	16	16	
	LiCdCl ₃ · 1/2 H ₂ O	C 426	In	Orth	Pnma	PD	108	17	17	
	TiCdCl ₃					aq			175	
	NH ₄ CdCl ₃	I 289	Co	Orth	Pnma	aq	206	16 18	175	
	(N ₂ H ₅)CdCl ₃					aq			172	
	CsSnCl ₃	C 270					129			
	RbSnCl ₃	C 228					129			
	KSnCl ₃	C 224					135			
	TiSnCl ₃	C 244					199			
	NH ₄ SnCl ₃ · H ₂ O					aq			173	
	N ₂ H ₅ SnCl ₃					Et OH			173	
	CsHgCl ₃		Co	Mon	P2 ₁ /m	aq		13	13	Pseudo Cubic
	KHgCl ₃	C 239	Co	Cub	Pm3m	aq		19 20	19 20	
	NaHgCl ₃					aq	109		174	
	THgCl ₃	C 224				aq		21	21	
	NH ₄ HgCl ₃	I 272	Co	Orth	Pnam	aq	200			
	N ₂ H ₅ HgCl ₃	157		Tet	P4/m	PD	109	22	22	
	CsPbCl ₃	C 590				CCl ₄ Et OH			174	
	RbPbCl ₃	C 440	Co	Cub	Pm3m	aq	119		177	
	TiPbCl ₃	I 397	In	Tet		aq	131	24 23	24 23	Above 49°C (24) Below 49°C (23)
	K ₂ Hg ₃ Cl ₈	I 199					109			
	(NH ₄) ₂ Hg ₃ Cl ₈					aq			174	
	TiHg ₂ Cl ₅	I 499					199			
	NaMn ₂ Cl ₅	I 441					105			
	CsZn ₂ Cl ₅	C 294					118			
	RbZn ₂ Cl ₅	C 306					118			
	KZn ₂ Cl ₅	C 274					125			
	TiZn ₂ Cl ₅	I 260					205			
	NH ₄ Zn ₂ Cl ₅	C 250					107			
	KSr ₂ Cl ₅	C 638					128			
	NH ₄ Cd ₂ Cl ₅	C 366					107			
	CsSn ₂ Cl ₅	I 224					129			
	RbSn ₂ Cl ₅	C 231					129			
	KSn ₂ Cl ₅	C 208					135			
	CsHg ₂ Cl ₅					aq			176	

Valency of Central Ion	Compound	Melting Pt., °C	Crystal Data			Preparation	Literature			Remarks
			Complete or Incomplete	Crystal Class	Space Group		Phase Diagram	Crystal Structure	Preparation	
II	KHg ₂ Cl ₅					aq			174	Prep uses EtOAc and NaHgCl ₃
	NaHg ₂ Cl ₅					special			174	
	NH ₄ Hg ₂ Cl ₅	I 214					109			
	CsPb ₂ Cl ₅					aq			177	
	RbPb ₂ Cl ₅	C 423				aq	131		177	
	KPb ₂ Cl ₅	C 440					125			
	TlPb ₂ Cl ₅	C 427					198			
	NH ₄ Pb ₂ Cl ₅		In	Orth		aq		4	4	
	CsMg ₃ Cl ₇	I 565					117			
	KSn ₃ Cl ₇	C 208					135			
	CsMn ₄ Cl ₉	I 537					112			
	NH ₄ Hg ₉ Cl ₁₉	I 235					109			
	CsHg ₅ Cl ₁₁					aq			176	
	RbHg ₅ Cl ₁₁					aq			176	
	KHg ₇ Cl ₁₅	I 209					109			
	NaClCaCl ₂ mixed Xstals					melt		53		
	LiCl-MnCl ₂ mixed Xstals					melt		51 52		
	(EtNH ₃) ₄ FeCl ₇	117°							188	
	(Me ₂ NH ₂) ₄ FeCl ₇	48°							188	
	(PrNH ₃) ₄ FeCl ₇	118°							188	
III	Cs ₃ ScCl ₆	C 815					143			From Rh, NaCl and CCl ₄ at 500°C
	Cs ₃ TiCl ₆	C 770					139			
	Rb ₃ TiCl ₆	C 794					139			
	K ₃ TiCl ₆	C 760					139			
	Na ₃ TiCl ₆	I 555					144			
	K ₃ VCl ₆	C 745					145			
	Na ₃ VCl ₆	C 535					145			
	K ₃ CrCl ₆	C 836					140			
	Na ₃ CrCl ₆	C 620					140			
	K ₃ MoCl ₆					aq			168	
	(NH ₄) ₃ MoCl ₆					aq			168	
	Na ₃ RhCl ₆					spec			169	
	Cs ₃ InCl ₆					conc HCl			179	
	Rb ₃ InCl ₆					conc HCl			179	
	Cs ₃ LaCl ₆	C 777					146			
	K ₃ LaCl ₆	C 625					146			
	Cs ₃ CeCl ₆	C 800					146			
	K ₃ CeCl ₆	C 628					146			
	Cs ₃ NdCl ₆	C 813					146			
	K ₃ NdCl ₆	C 682					146			
	K ₃ IrCl ₆					aq			186	
	Rb ₃ TiCl ₆					spec			179	From Cl ₂ concHCl, Ti ₂ O ₃ and RbCl
	Tl ₃ TiCl ₆		In	Hex	C31c	aq		68	69	
	Tl ₃ BiCl ₆	C 413					196			
	Rb ₃ UCl ₆	C 775					142			
	K ₃ PuCl ₆	C 685					147			
	L ₇ Bi ₃ Cl ₁₆		In	Hex		aq		71	71	
	K ₂ TiCl ₅	I 610					144			
	Cs ₂ VCl ₅					conc HCl			178	
	Rb ₂ VCl ₅					conc HCl			178	

Valency of Central Ion	Compound	Melting Pt., °C	Crystal Data			Preparation	Literature			Remarks
			Complete or Incomplete	Crystal Class	Space Group		Phase Diagram	Crystal Structure	Preparation	
III	(NH ₄) ₂ VCl ₅					conc HCl			178	
	Ti ₂ FeCl ₅	I 290					197			
	(Me ₂ NH ₂) ₂ FeCl ₅	98							188	
	(Me ₃ NH) ₂ FeCl ₅	143							188	
	(NH ₄) ₂ RuCl ₅					aq			185	
	K ₂ SbCl ₅					conc HCl			187	
	(NH ₄) ₂ SbCl ₅		Co	Mon	C2/m	aq		70	70	
	K ₂ CeCl ₅	C 623					146			
	K ₂ NdCl ₅	C 602					122			
	Cs ₂ TiCl ₅					conc HCl			180	
	Ti ₂ BiCl ₅	I 330					196			
	Rb ₂ UCl ₅	I 560					142			
	K ₂ UCl ₅	685					148			
	K ₂ PuCl ₅	I 611					147			
	K ₅ W ₃ Cl ₁₄					aq		170	170	Existence strongly indicated by x-ray powder diagrams
	Cs ₃ Sc ₂ Cl ₉	I 620					143			
	Cs ₃ Ti ₂ Cl ₉		In	Hex	P6 ₃ /mmc	spec		59	59	Grown over solid melt
	Cs ₃ V ₂ Cl ₉		In	Hex	P6 ₃ /mmc	spec		59	59	Grown over solid melt
	Cs ₃ Cr ₂ Cl ₉		Co	Hex	P6 ₃ /mmc	spec		59	59	Grown over solid melt
	Cs ₃ Fe ₂ Cl ₉		In	Hex	P3m1	aq		60	60	
	Cs ₃ As ₂ Cl ₉		Co	Hex	P32 P321	aq		61 62	61 62	
	Cs ₃ Sb ₂ Cl ₉		In	Hex	P3m1	aq		60	60	
	Rb ₃ Sb ₂ Cl ₉					HCl			187	
	K ₃ Sb ₂ Cl ₉	I 340					138			
	(NH ₄) ₃ Sb ₂ Cl ₉	C 291					138			
	Cs ₃ W ₂ Cl ₉		Co	Hex	C6 ₃ /m	aq		63 64	63 64	
	Rb ₃ W ₂ Cl ₉		In	Hex	C6 ₃ /m	aq		63 64	63 64	
	K ₃ W ₂ Cl ₉		Co	Hex	C6 ₃ /m	aq		63 64 65	63 64 65	
	(NH ₄) ₃ W ₂ Cl ₉		In	Hex	C6 ₃ /m	aq		63 64	63 64	
	Ti ₃ W ₂ Cl ₉		In	Hex	C6 ₃ /m	aq		63 64	63 64	
	Cs ₃ Ti ₂ Cl ₉		Co	Hex	R3c	aq		66 67	66 67	
	Cs ₃ Bi ₂ Cl ₉					aq			62	
	Ti ₃ Bi ₂ Cl ₉	I 225					196			
	CsBCl ₄		In			spec		54	54	Rhombohedral. From BCl ₃ and CsCl at elevated temp and pressure
	CsAlCl ₄	C 377				spec	136			
	KAICl ₄	C 256				spec	137			
	NaAlCl ₄	C 151	Co	Orth	P2 ₁ 2 ₁ 2 ₁	PD	137	55	55	
	LiAlCl ₄	I 143.5					138			
	TiAlCl ₄	C 297					138			
	(NH ₄)AlCl ₄	C 304				spec	138			
	CsTiCl ₄	C 781					139			
	RbTiCl ₄	C 806					139			
	KTiCl ₄	C 654					139			
	KVCl ₄					conc HCl			178	
	KFeCl ₄	C 249					140			

Valency of Central Ion	Compound	Melting Pt., °C	Crystal Data			Preparation	Literature			Remarks
			Complete or Incomplete	Crystal Class	Space Group		Phase Diagram	Crystal Structure	Preparation	
III	NaFeCl ₄	C 163					140			
	(NH ₄)FeCl ₄	C 295					107			
	(MeNH ₃)FeCl ₄	211							188	
	(Me ₂ NH ₂)FeCl ₄	101							188	
	(Me ₃ NH)FeCl ₄								188	
	(Me ₄ N)FeCl ₄	> 308							188	
	(EtNH ₃)FeCl ₄	85							188	
	(nPrNH ₃)FeCl ₄								188	
	(nBuNH ₃)FeCl ₄	605							188	
	(Ph ₄ As)FeCl ₄		In	Tet	I ₄ ⁻	aq		56	56	
	CsGaCl ₄	385 ⁰				spec			181	
	KGaCl ₄	259 ⁰				spec			181	
	NH ₄ GaCl ₄	304 ⁰				spec			181	
	(NH ₄)RuCl ₄ ·2H ₂ O					aq			185	Loses 2H ₂ O at 220°C
	NaInCl ₄	C 730					141			
	KSbCl ₄	I 114					138			
	NaSbCl ₄					from HCl			187	
	NH ₄ SbCl ₄	I 143					138			
	KICl ₄		Co	Mon	P2 ₁ /n	aq		57	57	
	KAuCl ₄		In	Mon	P2 ₁ /c	Et OH		58	58	
	TlAuCl ₄					aq			180	
	RbUCl ₄	I 470					142			
	TlAl ₂ Cl ₇	I 163					138			
	Tl _x Al _y Cl _(x+3y)	C 192					138			
	(NH ₄) _x Al _y Cl _(x+3y)	C 192.5					138			
	Cs ₂ AgAuCl ₆		Co Co	Cub Tet	I ₄ /mmm Pm3m	aq		15 162 163	15 162 164	Fresh prepared Diamagnetic Aged
	Cs ₂ AuAuCl ₆		Co Co	Cub Tet	Pm3m I ₄ /mmm	aq		164 162 162	164 162 162	Aged Aged - CsAuCl ₃
	Cs ₄ Cu(AuCl ₆) ₂		In	Cub	(Im3m?)	aq		165 164	165	
	Cs ₄ Zn(AuCl ₆) ₂		In	Cub	(Im3m?)	aq		164	164	
	Cs ₄ Cd(AuCl ₆) ₂		In	Cub	(Im3m?)	aq		164	164	
	Cs ₄ Hg(AuCl ₆) ₂		In	Cub	(Im3m?)	aq		164	164	
	Cs ₄ Pd(AuCl ₆) ₂		In	Cub	(Im3m?)	aq		165	165	
	Rb ₄ Cu(AuCl ₆) ₂		In	Cub	(Im3m?)	aq		165	165	
	Rb ₄ Pd(AuCl ₆) ₂		In	Cub	(Im3m?)	aq		165	165	
	Cs ₂ Ag _y Au _{1-y} AuCl ₆		In	Cub	(Im3m?)	aq		166	166	
	Rb ₆ Ag ₂ Au ₃ Cl ₁₇		In	Orth		aq		167	167	
	(NH ₄) ₆ Ag ₂ Au ₃ Cl ₁₇		In	Orth		aq		167	167	
	Ag ₂ Cu ₄ Au ₂ Cl ₁₂		In	Cub	(Im3m?)	aq		164	164	
IV	Na ₄ ZrCl ₈	C 535					149			
	K ₃ ZrCl ₇	I* 532					150			I* 532, Compd. decomposes in solid state
	Na ₃ ZrCl ₇	I 530					155			
	Cs ₃ ThCl ₇	C 720					207			
	K ₃ ThCl ₇	C 705					207			
	Cs ₂ TiCl ₆	570	Co	Cub	Fm3m	aq spec		72	72 182	
	Rb ₂ TiCl ₆	605	Co	Cub	Fm3m	aq spec		72	72 182	
	(NH ₄) ₂ TiCl ₆		Co	Cub	Fm3m	aq		73	73	
	Cs ₂ GeCl ₆		Co	Cub	Fm3m	aq		74	74	
	Cs ₂ SeCl ₆		Co	Cub	Fm3m	aq		72	72	
	Rb ₂ SeCl ₆		Co	Cub	Fm3m	aq		72	72	

Valency of Central Ion	Compound	Melting Pt., °C	Crystal Data			Preparation	Literature			Remarks
			Complete or Incomplete	Crystal Class	Space Group		Phase Diagram	Crystal Structure	Preparation	
IV	(NH ₄) ₂ SeCl ₆		Co	Cub	Fm3m	aq		72	72	
	Cs ₂ ZrCl ₆	C 805	Co	Cub	Fm3m	aq	150	72	72	
	Rb ₂ ZrCl ₆		Co	Cub	Fm3m	aq		72	72	
	K ₂ ZrCl ₆	C 798					150			
	Na ₂ ZrCl ₆	C 700					151			
	Cs ₂ RuCl ₆		In	Cub	Fm3m	aq		75	185 75	
	Rb ₂ RuCl ₆					aq			185	
	K ₂ RuCl ₆		Co	Cub	Fm3m	aq		76	185 76	
	Cs ₂ RhCl ₆		In	Cub	Fm3m	aq		77	77	
	Cs ₂ PdCl ₆		In	Cub	Fm3m	aq		78	78	
	Rb ₂ PdCl ₆		In	Cub	Fm3m	aq		78	78	
	K ₂ PdCl ₆		Co	Cub	Fm3m	aq		78	78	
	(NH ₄) ₂ PdCl ₆		In	Cub	Fm3m	aq		78	78	
	(RNH ₃) ₂ PdCl ₆					aq		78	78	R = Me, Et, nPr, Iso-Pr., nButyl, isobutyl, isoamyl, pyridinium, MePy, Me ₂ Py, Me ₃ Py, isoquinoline
	(R ₂ NH ₂) ₂ PdCl ₆					aq		78	78	
	(R ₃ NH) ₂ PdCl ₆					aq		78	78	
	(R ₄ N) ₂ PdCl ₆					aq		78	78	
	Cs ₂ SnCl ₆		Co	Cub	Fm3m	aq		72 79	72 79	
	Rb ₂ SnCl ₆		Co	Cub	Fm3m	aq		72 79	72 79	
	K ₂ SnCl ₆		Co	Cub	Fm3m	aq		80	80	
	Tl ₂ SnCl ₆		Co	Cub	Fm3m	aq		72	72	
	(NH ₄) ₂ SnCl ₆		Co	Cub	Fm3m	aq		72 80	72 80	
	(MeNH ₃) ₂ SnCl ₆		Co	Hex	R3m	aq		81	81	
	(Me ₂ NH ₂) ₂ SnCl ₆		Co	Orth	Pn2m	aq		82	82	
	(Me ₂ Et ₂ N) ₂ SnCl ₆		Co	Tet	P4nc	aq		83	83	
	(Me ₃ NH) ₂ SnCl ₆		Co	Cub	Th6	aq		84	84	
	(Me ₄ N) ₂ SnCl ₆		Co	Cub	Fm3m	aq		84	84	
	(EtNH ₃) ₂ SnCl ₆		Co	Hex	P3m1	aq		85	85	
	Rb ₂ SbCl ₆		Co	Cub	Fm3m	aq		86 87	86 87	
	Cs ₂ TeCl ₆		Co	Cub	Fm3m	aq		72 79	72 79	
	Rb ₂ TeCl ₆		Co	Cub	Fm3m	aq		72 79	72 79	
	K ₂ TeCl ₆		Co Co	Cub Mon	Fm3m 2/m	aq		72	72	Pseudocubic
	(NH ₄) ₂ TeCl ₆		Co	Cub	Fm3m	aq		72	72	
	Tl ₂ TeCl ₆		Co	Cub	Fm3m	aq		72	72	
	(N(CH ₃) ₄) ₂ CeCl ₆		Co	Cub	Fm3m	aq		88	88	
	(PyH ⁺) ₂ CeCl ₆					MeOH			189	
	(Quin) ₂ CeCl ₆					MeOH			189	
	Cs ₂ HfCl ₆	C 820				PD	150		150	
	K ₂ HfCl ₆	C 803				PD	150		150	
	Na ₂ HfCl ₆	C 560				PD	150		150	
	K ₂ ReCl ₆		Co	Cub	Fm3m	aq		89	89	
	(NH ₄) ₂ ReCl ₆					aq		89	89	
	Cs ₂ OsCl ₆		In	Cub	Fm3m	aq		75	75	
	Rb ₂ OsCl ₆					aq			186	
	K ₂ OsCl ₆		Co	Cub	Fm3m	aq		90	90	
	(NH ₄) ₂ OsCl ₆					aq			186	
	K ₂ IrCl ₆					aq		91	91	

Valency of Central Ion	Compound	Melting Pt., °C	Crystal Data			Preparation	Literature			Remarks
			Complete or Incomplete	Crystal Class	Space Group		Phase Diagram	Crystal Structure	Preparation	
IV	(NH ₄) ₂ IrCl ₆		In	Cub	Fm3m	aq		91	91	
	Cs ₂ PtCl ₆		Co	Cub	Fm3m	aq		72 79/92	72 79/92	
	Rb ₂ PtCl ₆		Co	Cub	Fm3m	aq		72 79 92	72 79 92	
	K ₂ PtCl ₆		Co	Cub	Fm3m	aq		72 93 94	72 93 94	
	(NH ₄) ₂ PtCl ₆		Co	Cub	Fm3m	aq		72	72	
	(NH ₃ CH ₃) ₂ PtCl ₆		In	Hex	R3m	aq		81	81	
	(NiCH ₃) ₄ 2PtCl ₆		Co	Cub	Fm3m	aq		95	95	
	(NH ₃ (C ₂ H ₅) ₂) ₂ PtCl ₆		In	Cub	D3m1	aq		85	85	
	Ti ₂ PtCl ₆		Co	Cub	Fm3m	aq		72	72	
	Cs ₂ PbCl ₆		Co	Cub	Fm3m	aq		72 79	72 79	
	Rb ₂ PbCl ₆		Co	Cub	Fm3m	aq		72 79	72 79	
	(NH ₄) ₂ PbCl ₆					aq		79	79	
	Cs ₂ ThCl ₆	I 573	Co	Hex	C3m		207	97		
	K ₂ ThCl ₆	I 406					207			
	Na ₂ ThCl ₆	C 360					207			
	Cs ₂ UCl ₆	C 680	Co	Hex	C3m			97		
	K ₂ UCl ₆	C 655				PD	152		152	
	Na ₂ UCl ₆	C 440				PD	152		152	
	Li ₂ UCl ₆	C 420				PD	155		154	
	(NiCH ₃) ₄ 2UCl ₆		In	Cub	Fm3m	aq		98	98	
	(NiC ₂ H ₅) ₄ 2UCl ₆		In	Orth Cu	Fmmm Fm3m	aq		98	98	Below 94°C Above 94°C
	Cs ₂ PuCl ₆		Co	Hex	C3m	aq		99	99	
	(NiCH ₃) ₄ 2PuCl ₆		In	Cu	Fm3m	aq		98	98	
	(NiC ₂ H ₅) ₄ 2PuCl ₆		In	Orth Cub	Fmmm Fm3m			98	98	Below 97°C Above 97°C
	Cs ₂ 50% + Rb ₂ 44% PtCl ₆			Cub	Fm3m	aq		96	96	Compl. Misc.
	Cs ₂ PtCl ₆ 50% Cs ₂ TeCl ₆ 50%			Cub	Fm3m	aq		92	92	Compl. Misc.
	NaZrCl ₅	C 330				PD	149		149	
	NH ₄ PbCl ₅					spec			191	From PbCl ₄ and NH ₄ Cl
	CsThCl ₅	C 490					207			
	KThCl ₅	C 428					207			
	NaThCl ₅	I 370				aq	207		190	
	KUCl ₅	I 360				PD	142		142	
	Na ₃ Zr ₄ Cl ₁₉	I 380				PD	155		155	
	NaZr ₂ Cl ₉	I 317				PD	150		150	
	CsU ₂ Cl ₉	I 390				PD	142		142	
	KU ₃ Cl ₁₃	I 390				PD	142		142	
V	CsNbCl ₆	C 528				PD	153		153	
	RbNbCl ₆	I 360				PD	153		153	
	KNbCl ₆	C 400				PD	153		153	
	NaNbCl ₆	I 458				PD	153		153	
	NH ₄ NbCl ₆	I 272				PD	154		154	
	CsTaCl ₆	C 555				PD	153		153	
	RbTaCl ₆	C 416				PD	153		153	

Valency of Central Ion	Compound	Melting Pt., °C	Crystal Data			Preparation	Literature			Remarks
			Complete or Incomplete	Crystal Class	Space Group		Phase Diagram	Crystal Structure	Preparation	
V	KTaCl ₆	I 420				PD	153		153	
	NaTaCl ₆	I 470				PD	153		153	
	LiTaCl ₆	I 350				PD	153		153	
	NH ₄ TaCl ₆	C 304				PD	154		154	
	Cs ₄ FeSbCl ₁₂		In	Cub		aq		87		
	Rb ₄ FeSbCl ₁₂		In	Cub		aq		87		
	K ₄ FeSbCl ₁₂		In	Cub		aq		87		
	(NH ₄) ₄ FeSbCl ₁₂		In	Cub Tet	P4/mmm	aq		87		Fresh prep. Aged
	(NH ₄) ₄ InSbCl ₁₂		In	Cub		aq		87		
	(NH ₄) ₄ TlSbCl ₁₂		In	Cub		aq		87		

Remarks:

The compounds are listed according to

- valency;
- formula type, in the general order A_xB_yCl_z, A > B to A < B;
- atomic number of the central ion (within each formula type);
- in the order Cs, Rb, K, Na, Li, Tl, NH₄, substituted amines, others;
- compounds with the ion AuCl₆³⁻ or M^{III}SbCl₁₂⁴⁻ are listed together.

Abbreviations:

- PD Phase Diagram
- I Incongruent melting
- C Congruent melting
- In Incomplete
- Co Complete
- Mon Monoclinic
- Orth Orthorhombic
- Tet Tetragonal
- Hex Hexagonal
- Cub Cubic
- aq From aqueous (or acidified) solution
- H₂O Anhydrous compound can be obtained by heating or dehydration under vacuum

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