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STAUFFER CHEMICAL COMPANY

HIGH ENERGY OXIDIZERS

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Project NR 093-035

Western Research Center
Richmond, California

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ARPA No. 399-62

OFFICE OF NAVAL RESEARCH

WASHINGTON, D. C.

Quarterly Technical Summary Report

for the Period February 1, 1965 to April 30, 1965

Investigators

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Foreword

This is the first Quarterly Technical Summary Report of the third year's investigation of complexes based on chlorinefluorides. It covers the period from February 1, 1965 to April 30, 1965. The work was conducted at the Western Research Center, Richmond, California, Stauffer Chemical Company, under the sponsorship of the Advanced Research Projects Agency. The work was administered by the Department of the Navy, Office of Naval Research, with Mr. R. L. Hansen serving as Scientific Officer, under ARPA No. 399-62.

The report is presented in the form of a paper to be published in Inorganic Chemistry, 1965.

Contribution from the Western Research Center

Stauffer Chemical Company, Richmond, California

Difluorochlorates(I) of Cesium, Rubidium, and Potassium

By Karl O. Christe and Jacques P. Guertin

Abstract

The difluorochlorates(I) of cesium, rubidium, and potassium were successfully prepared by the reaction of the corresponding fluorides with chlorine monofluoride or $NO^+ClF_2^-$. These white crystalline solids are the first known difluorochlorate(I) salts stable at 25°. They decompose exothermically at temperatures higher than 230°. Their composition and structure were established by elemental analysis, infrared, and X-ray studies. The salts are ionic, contain linear ClF_2^- anions, and crystallize tetragonally in the α-KHF_2 lattice type. The unit cell dimensions of $CsClF_2$, $RbClF_2$, and $KClF_2$ are: a = 6.10 Å., c = 7.78 Å., a = 5.88 Å., c = 7.23 Å., a = 5.63 Å., c = 6.72 Å., respectively. Attempts to prepare $LiClF_2$ and $Ca(ClF_2)_2$ failed, while $NaClF_2$, $Ba(ClF_2)_2$, and $Sr(ClF_2)_2$ may have formed to a very small extent.

Introduction

The existence of ionic complexes containing species such as ClF_2^+ [1-5] and ClF_4^- [6-9], derived from chlorine trifluoride, is well established. However, complexes containing such species as Cl^+ and ClF_2^-, formed from chlorine monofluoride, have not been investigated until recently. Schmeisser[10] isolated $Cl^+AsF_6^-$ and

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(1) F. Seel and O. Detmer, Angew. Chem., 70, 163 (1958).

(2) F. Seel and O. Detmer, Z. anorg. allgem. Chem., 301, 113 (1959).

(3) N. Bartlett and D. H. Lohmann, J. Chem. Soc., 5253 (1962).

(4) H. Selig and J. Shamir, Inorg. Chem., 3, 294 (1964).

(5) K. O. Christe and A. E. Pavlath, Z. anorg. allgem. Chem., 335, 210 (1965).

(6) L. B. Asprey, J. L. Margrave, and M. E. Silverthorn, J. Am. Chem. Soc., 83, 2955 (1961).

(7) D. H. Kelly, B. Post, and R. W. Mason, J. Am. Chem. Soc., 85, 307 (1963).

(8) E. Whitney, R. MacLaren, C. Fogle, and T. Hurley, J. Am. Chem. Soc., 86, 2583 (1964).

(9) E. Whitney, R. MacLaren, T. Hurley, and C. Fogle, J. Am. Chem. Soc., 86, 4340 (1964).

(10) Summary Report on the Inorganic Fluorine Chemistry Meeting, Argonne, 1963, Science, 143, 1058 (1964).

$Cl^+SbF_6^-$, prepared by the interaction of ClF with the corresponding Lewis acid, AsF_5 or SbF_5. We[11] have reported the existence of the ClF_2^- anion in the form of its nitrosyl salt, $NO^+ClF_2^-$. Nitrosyl difluorochlorate(I) was shown to be ionic in solution and in the solid state. The ClF_2^- anion was assigned a linear structure based on infrared investigation. Since $NO^+ClF_2^-$ is stable only at low temperature we have investigated the replacement of the NO^+ cation by an alkali or alkaline earth metal cation with the hope of obtaining more stable complex salts. This paper describes the results obtained from (1) the metathetical reaction shown by the equation,

$$NO^+ClF_2^- + M^+F^- \longrightarrow M^+ClF_2^- + NOF \qquad (1)$$

and (2) the direct reaction shown by the equation,

$$ClF + M^+F^- \longrightarrow M^+ClF_2^- \qquad (2)$$

where M^+ is an alkali metal cation.

Experimental

Materials and Apparatus. - The materials used in this work were manipulated in a standard pyrex-glass high-vacuum system which which had stopcocks and joints lubricated with Halocarbon grease (high-temperature grade). Reactions at overatmospheric pressure

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(11) K. O. Christe and J. P. Guertin, Inorg. Chem., 4, in press (1965).

and elevated temperature were done in Monel containers equipped with a Monel pressure gauge and a Monel valve (Whitey, M6TS6). This valve could be connected to the glass vacuum line by Swagelock fittings and Kovar metal to graded glass seals. Chlorine monofluoride, nitrosyl fluoride (both from Ozark-Mahoning Company), and hexafluoroacetone (Allied Chemical) were purified by several low-temperature vacuum distillations. The purity of the volatile starting materials was determined by measurement of their vapor pressures, molecular weights, and infrared spectra. Little etching of the vacuum line could be observed. The alkali and alkaline earth metal fluorides (obtained from chemical supply houses) were used without further purification. Hygroscopic non-volatile compounds were handled in the dry nitrogen atmosphere of a glove box.

Infrared Spectra. - Infrared spectra were recorded on a Beckman Model IR-9 grating spectrophotometer in the range 4000-420 cm^{-1}. Screw cap metal cells equipped with neoprene O-rings and AgCl windows were used for solid samples. The solids were either mulled with dry hexafluorobenzene or dry nujol, or they were used directly as dry powders.

X-ray Powder Data. - Debye-Scherrer powder patterns were taken using a Philips Norelco Instrument, Type No. 12046, with Cu K_α radiation and a Ni filter. Samples were sealed in Lindeman glass tubes ($\sim$0.5 mm O.D.).

Differential Thermal Analysis. - A Perkin-Elmer differential scanning calorimeter Model DSC 1 was used to obtain the DTA of the new compounds. These were sealed in aluminum pans. A heating rate of 10°/min. and an argon purge of 30 ml./min. was used.

Elemental Analysis. - Products were analyzed for fluorine, chlorine, and alkali or alkaline earth metal. Fluorine was determined by direct alkaline hydrolysis or by Parr bomb fusion of the sample, each followed by titration with $ThNO_3$ using alizarine red as indicator. Chlorine was reduced to Cl^- either by Parr bomb fusion with Na_2O_2 or by direct alkaline hydrolysis of the sample followed by reduction with $TiSO_4$. Finally, the resultant Cl^- was potentiometrically titrated with $AgNO_3$. Both methods compared favorably, yielding results with negligible deviations. The alkali metal content was determined by direct aqueous hydrolysis of the sample followed by flame spectroscopy. Gravimetric analysis yielded the alkaline earth metal content of a sample.

Preparation of the Alkali Metal Difluorochlorates(I) - Chlorine monofluoride and an alkali metal fluoride were mixed under different conditions at temperatures from 25 to 230° under autogenous pressures. In some reactions agitation and/or NOF (as a catalyst) were employed. Also, CsF was sometimes pretreated with CF_3COCF_3.

In a typical experiment, CsF (0.204 mole) was introduced into a 300 ml. Monel cylinder having NPT openings (0.5 in.) on both ends to facilitate removal of solid products. One end of the cylinder

was capped with a Swagelock fitting and the other end was connected by Monel high-pressure tubing to a Monel pressure gauge (0-2000 p.s.i.) and a Monel control valve (Whitey, M6TS6). The cylinder was connected to the vacuum system and CF_3COCF_3 (0.350 mole) was condensed into it. The mixture was vigorously shaken for 12 hours at 25° under autogenous pressure, after which all volatile material was removed by vacuum pumping on the cylinder (warmed to 150°) for two hours. Now, excess ClF (0.700 mole) was condensed at -196° over the CsF. The mixture was heated for 48 hours at 175° in an electric tube furnace equipped with an automatic temperature control. An internal pressure of 800 p.s.i. developed. After cooling to 25°, the volatile material was similarly removed (except in this case the cylinder was warmed only to 100°). The non-volatile, white, crystalline product was removed from the cylinder and the increase in weight of the starting material (CsF) was determined (Table I).

Results and Discussion

Synthesis. - The difluorochlorates(I) of Cs, Rb, and K were successfully prepared by (1) metathetical reaction, or (2) direct interaction of ClF with the corresponding fluoride. Table I lists the results of several experiments. A 100% conversion of starting material to the difluorochlorate(I) was never achieved. After reaction at elevated temperature and pressure, the product usually was a fused solid and was difficult to remove from the reactor.

TABLE I

Syntheses of $CsClF_2$, $RbClF_2$, and $KClF_2$[a]

Reactants, moles			Reaction Temperature, °C	Reaction Time, Hours	Reaction Pressure, p.s.i.	Conversion to ClF_2^- salt based on weight increase of starting material, %	Calcd., %[b]			Found, %		
Fluoride	ClF	NOF					Metal	Cl	F	Metal	Cl	F
CsF							Cs					
0.200[c]	0.700	-	175	48	800	55	74.8	9.4	15.8	73.6	9.1	16.0
0.035	0.210	0.012	175	48	1100	80	69.0	13.7	17.2	69.5	8.7	17.4
RbF							Rb					
0.047[d]	0.200	0.047	25	24	1100	49	68.1	10.9	21.0	68.1	10.8	20.7
0.036	0.220	-	230	60	1300	73	61.4	16.3	22.4	60.6	15.0	22.3
0.028[e]	0.240	0.015	230	60	1580	87	57.4	19.4	23.2	58.2	8.2	22.4
KF							K					
0.069	0.390	0.031	150	14	2200	27	58.5	8.5	33.0	58.2	8.5	33.7

[a] All reactions were done in 30 ml. Monel cylinders, except the first row reaction (done in a 300 ml. Monel cylinder).

[b] Calculated from the weight increase of the starting material assuming the product to be a ClF_2^-/F^- mixture only.

[c] CsF was pretreated with excess CF_3COCF_3 at 25°.

[d] This mixture was vigorously agitated.

[e] A small amount of Rb_2NiF_6 impurity caused the product to have a slight pink color.

The temperature of reaction could not be increased much higher than 230° due to the limited thermal stability of the products and interaction of the compounds with the Monel reactor resulting in the formation of some dark red alkali metal hexafluoronickelate(IV). This impurity was easily identified by its known X-ray diffraction pattern[12-15] and by analysis of the product for Ni.

No difficulties were expected for the metathetical reaction. The low thermal stability of $NO^+ClF_2^-$ [11] assured the complete removal of the complex from the product. Since NOF is regenerated during the reaction [equation (1)], only catalytic amounts are required. Generally, the use of NOF resulted in higher conversions of the starting material; however, analyses indicated too low a Cl content compared with the alkali metal and F content and the per cent conversion found from the weight increase of starting material. Therefore, the reaction of CsF with NOF in the absence of ClF was investigated. A relatively stable adduct was formed, the diffraction pattern of which was similar to that obtained for $CsClF_2$. Consequently, identification of this adduct in the presence of $CsClF_2$ was difficult. The formation of a CsF-NOF adduct, and the fact that

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(12) W. Klemm and E. Huss, Z. anorg. allgem. Chem., 258, 221 (1949).

(13) H. Bode, Naturwissenschaften, 37, 477 (1950).

(14) I. R. Scholder and W. Klemm, Angew. Chem., 66, 461 (1954).

(15) H. Bode and E. Voss, Z. anorg. allgem. Chem., 286, 136 (1956).

the formula weight of an NO group is roughly equal to the atomic weight of a Cl atom, rationalizes the analytical results. In several experiments the CsF was pretreated with excess CF_3COCF_3. However, no significant activation effect was observed. On this basis, the direct reaction of ClF with the corresponding alkali metal fluoride seems to be the preferred method for preparing the difluorochlorate(I) salts.

The difluorochlorates(I) of Li and Ca could not be prepared at 25 and 150° even using high autogenous ClF pressures (~2000 p.s.i.). No weight increase of the starting material was observed and the X-ray diffraction pattern showed no new products. Similarly, the reaction of NaF with ClF at 25° yielded negative results. Increasing the reaction temperature to 150° and using NOF as a catalyst resulted in a slight weight increase of the starting material. Also, the X-ray diffraction pattern revealed a few additional weak lines. However, analysis indicated no Cl in the product. From similar observations, SrF_2 and BaF_2 reacted with a mixture of ClF and NOF at 25 and 150° to an equally small extent. Again, no Cl was found in the product. The greater tendency of CsF, RbF, and KF to form stable complex salts compared with the other alkali and alkaline earth metal fluorides was also observed in the case of tetrafluorochlorates(III)[6-8] and salts containing the CF_3O^- anion[16].

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(16) D. C. Bradley, M. E. Redwood, and C. J. Willis, Proc. Chem. Soc., 416 (1964).

Properties of Cs, Rb, and K difluorochlorate(I)[17]. - The compounds are white crystalline solids having good thermal stability. Differential thermal analysis indicated exothermic decompositions at 262, 248, and 237°, respectively. This stability order, $CsClF_2$ > $RbClF_2$ > $KClF_2$, follows the same sequence found for the ClF_4^- [8] and CF_3O^- [16] alkali salts. The decrease in cation size and the increase in polarizing power from Cs^+ to Li^+ [18] (in Group 1a of the periodic table of elements) probably accounts for this order of stability. By comparison, the difluorochlorates(I) have lower oxidizing power and are somewhat less stable than the corresponding tetrafluorochlorates(III)[6-8]. This is in agreement with the reported stabilities of $NO^+ClF_2^-$ and $NO^+ClF_4^-$ [11].

Structure of Cs, Rb, and K difluorochlorates(I). - The infrared spectrum of $CsClF_2$ in the range 4000 to 420 $cm.^{-1}$ showed its

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(17) These compounds were not obtained pure. They invariably contained a certain percentage of the corresponding fluoride due to incomplete conversion of the starting material. Therefore, the properties given refer to difluorochlorate(I)/fluoride mixtures.

(18) I. G. Ryss, "The Chemistry of Fluorine and its Inorganic Compounds", State Publishing House for Scientific, Technical, and Chemical Literature, Moscow (1956), English translation, Vol. 1, 1960, p. 217.

strongest absorption at 636 cm.$^{-1}$ in agreement with the 635 cm.$^{-1}$ value found for the asymmetric stretching of the ClF_2^- anion in $NO^+ClF_2^-$ [11]. Based on the suggested linearity of the ClF_2^- anion in $NO^+ClF_2^-$, a similar structure is assumed for the ClF_2^- anion in the alkali metal difluorochlorates(I).

The X-ray diffraction patterns of $CsClF_2$, $RbClF_2$, and $KClF_2$ indexed tetragonally (Table II) resulting in the following unit cell dimentions:

	a, Å	c, Å	c/a
$CsClF_2$	6.10	7.78	1.275
$RbClF_2$	5.88	7.23	1.230
$KClF_2$	5.63	6.72	1.195

Comparison of these X-ray diffraction patterns with those reported for the α-modification of $CsHF_2$, $RbHF_2$, and KHF_2 [19,20], reveals that all crystallize tetragonally, have similar unit cell dimensions, and show diffraction lines of similar intensities. This is not so surprising since both the HF_2^- and ClF_2^- anions are linear and their sizes may not be much different. In addition, the contribution of

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(19) R. Kruh, K. Fuwa, and T. E. McEver, J. Am. Chem. Soc., 78, 4256 (1956).

(20) "Powder Diffraction File", ASTM Special Technical Publication 48-M2, American Society for Testing and Materials, Philadelphia, U.S.A., No. 1-1095 (1964).

TABLE II

X-Ray Diffraction Data

$CsClF_2$				$RbClF_2$				
hkl	d Obsd.	d Calcd.	I Obsd.	hkl	d Obsd.	d Calcd.	I Obsd.	h
110	4.31	4.32	s	110	4.16	4.12	vs	1
002	3.88	3.89	mw	002	3.61	3.62	mw	0
200	3.04	3.05	ms	200	2.94	2.94	s	2
112	2.88	2.89	vs	112	2.72	2.73	vs	1
211	2.57	2.57	w	211	2.46	2.47	m	2
202	2.40	2.40	s	202	2.278	2.280	s	2
220	2.157	2.157	ms	220	2.073	2.079	m	2
004	1.942	1.946	w	310	1.856	1.859	ms	3
310	1.927	1.929	ms	004	1.804	1.808	ms	2
222	1.889	1.886	ms	222		1.802		2
213		1.880		114	1.653	1.658	ms	3
114	1.775	1.773	m	312		1.653		1
312	1.731	1.728	ms	204	1.539	1.540	mw	3
204	1.643	1.640	m	400	1.467	1.470	vw	2
400	1.528	1.525	vw	224	1.362	1.364	m	4
411	1.459	1.454	vw	402		1.362		4
224	1.445	1.445	mw	420	1.311	1.315	w	3
402	1.425	1.420	mw	314	1.294	1.296	ms	3
314	1.373	1.370	ms	332		1.294		
215	1.352	1.352	mw	422	1.235	1.252	mw	
332		1.349		116	1.157	1.157	w	
422	1.291	1.287	m					
413		1.285						
116	1.246	1.242	mw					
404	1.200	1.200	mw					

TABLE II

X-Ray Diffraction Data

$RbClF_2$				$KClF_2$			
hkl	d Obsd.	d Calcd.	I Obsd.	hkl	d Obsd.	d Calcd.	I Obsd.
110	4.16	4.12	vs	110	3.97	3.98	ms
002	3.61	3.62	mw	002	3.34	3.36	mw
200	2.94	2.94	s	200	2.81	2.81	ms
112	2.72	2.73	vs	112	2.57	2.57	vs
211	2.46	2.47	m	211	2.36	2.36	s
202	2.278	2.280	s	202	2.159	2.158	s
220	2.073	2.079	m	220	1.991	1.989	mw
310	1.856	1.859	ms	310	1.785	1.780	s
004, 222	1.804	1.808, 1.802	ms	222	1.717	1.713	mw
				213	1.662	1.674	mw
114, 312	1.653	1.658, 1.653	ms	312	1.576	1.573	vw
				114	1.554	1.548	vw
204	1.539	1.540	mw	321	1.535	1.521	w
400	1.467	1.470	vw	204	1.453	1.442	vvw
224, 402	1.362	1.364, 1.362	m	402	1.305	1.298	w
				420	1.266	1.259	vvw
420	1.311	1.315	w	332	1.241	1.234	w
314, 332	1.294	1.296, 1.294	ms	314	1.228	1.222	mw
422	1.235	1.252	mw				
116	1.157	1.157	w				

the anions to the diffraction line intensities is relatively small when compared with that of the cations. Therefore, it is suggested that $CsClF_2$, $RbClF_2$, and $KClF_2$ possess the same crystal structure as α-$CsHF_2$, α-$RbHF_2$, and α-KHF_2, respectively. Figures 1a and 1b show this proposed structure.

The linear configuration of the ClF_2^- anion, supported by infrared and X-ray structural analyses, may be explained by either of the following models:

(i) a hybridization model[21], assuming mainly sp^3d-hybridization of the orbitals of the Cl atom resulting in a trigonal bipyramid with the two F atoms at the apexes, the Cl atom at the center, and the three free electron-pairs at the remaining corners,

or perhaps more probably

(ii) a semi-empirical molecular orbital model[21] involving mainly $p\sigma$ atomic orbitals for the formation of semi-ionic bonds.

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(21) J. G. Malm, H. Selig, J. Jortner, and S. A. Rice, Chem. Rev. 199 (1965).

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June 1, 1965

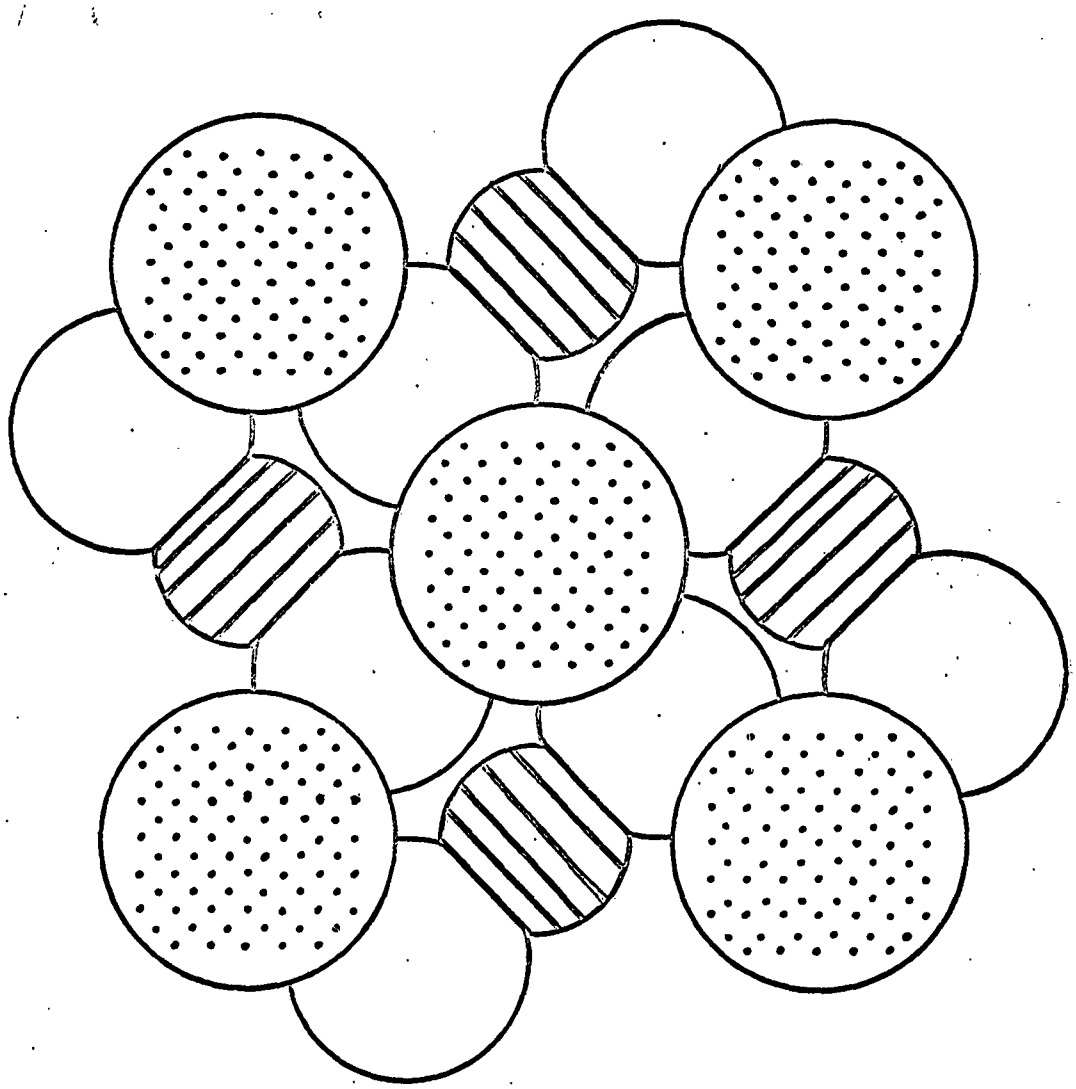

Fig. 1a .... A packing drawing showing the distribution of atoms in $CsClF_2$. Large dotted circles are Cs atoms; small striped circles are Cl atoms; blank circles are F atoms.

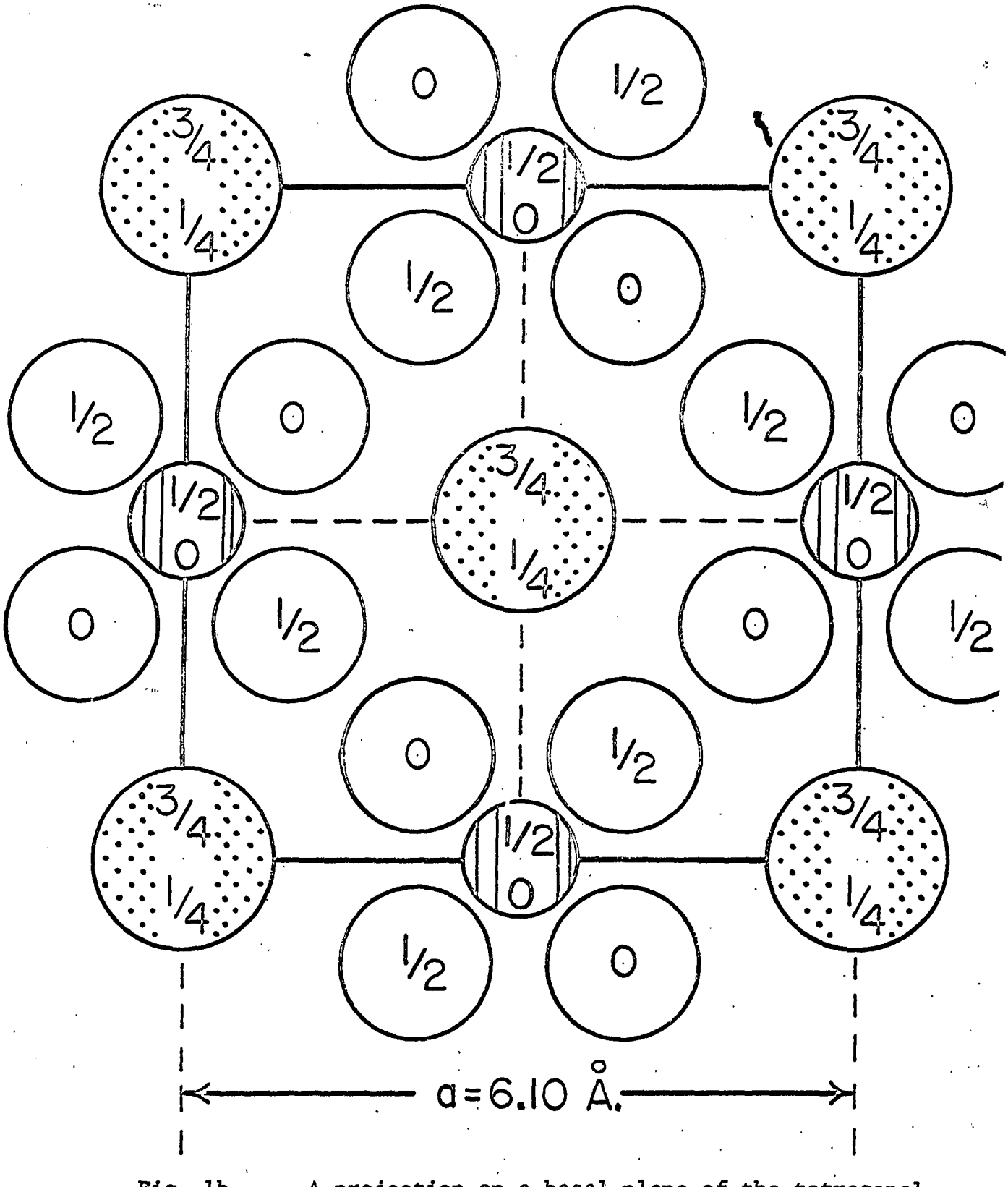

Fig. 1b .... A projection on a basal plane of the tetragonal structure of $CsClF_2$ (Fig. 1a). Circles represent atoms as described in Fig. 1a.

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