[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE 39, MASSACHUSETTS]

# The Preparation, Structures and Infrared Absorption of Salts of Cobalt(III) Hexafluoride Ion

BY M. D. MEYERS AND F. A. COTTON

RECEIVED MARCH 9, 1960

The preparation of salts of $CoF_6^{-3}$ by fluorination of the corresponding $Co(CN)_6^{-3}$ salts (Klemm and Huss' method) is described in detail. X-Ray and infrared studies of $K_2NaCoF_6$, $K_3CoF_6$, $Na_3CoF_6$, $Li_3CoF_6$ and $Ba_3[CoF_6]_2$ lead to the conclusion that only the first is rigorously cubic, whereas the remaining ones show increasing distortion of the lattice and the $CoF_6^{-3}$ octahedra in the order listed. Comparisons of the structures and infrared spectra with those of the corresponding aluminum compounds are made.

## Introduction

The spin-free $3d^6$ system occurs, in stable compounds, only in spin-free Fe(II) compounds, which are relatively numerous, and in the $[CoF_6]^{-3}$ ion.[1] In carrying out an investigation of the dynamic Jahn–Teller effect in such systems, which is reported separately,[2] we had occasion to prepare some salts of the $[CoF_6]^{-3}$ anion with various cations. Several of those described here have been reported before while two are new. In all cases we have examined (or reëxamined) the X-ray powder pictures and the infrared spectra, since these data give information on structure and symmetry vital to the interpretation of data on the electronic spectra and magnetic properties of the substances. We also report our preparative and analytical data for the known as well as the new compounds in some detail for two reasons. While the preparative method is not original with us, it has not, so far as we know, been described in any detail before, nor have analytical details indicating the purity of samples previously subjected to certain physical measurements been reported. Since we shall report magnetic results and certain X-ray data somewhat at variance with those previously given, as well as new infrared data, we feel obliged to justify our confidence in our own results.

$K_3CoF_6$ has been prepared previously by several methods. There is a "wet" method[3] which involves electrolytic oxidation of $CoF_2$ in concd. aqueous HF to give $CoF_3 \cdot 7/2H_2O$ followed by treatment of this with solid KF at −10°. This same method failed[4] to give $(NH_4)_3CoF_6$ when $NH_4F$ was used in place of KF. Klemm and co-workers have devised several sorts of "dry" methods. One general method[5] involves fluorinating a physical mixture of $CoCl_2$ with some salt containing the cation desired in the final product, *e. g.*, $3KCl + CoCl_2$ to get $K_3CoF_6$. A still better method involves fluorinating a complex salt differing from the desired product only in the ligands in the anion, *e. g.*, $K_3Co(CN)_6$ to get $K_3CoF_6$. This method has the advantage of being more likely to produce a homogeneous sample of a true chemical compound.

## Discussion

**Preparations.**—Hoppe and Klemm[6,7] have reported the preparation of $K_3CoF_6$ as well as the corresponding Li, Na, Rb and Cs compounds by this method but only in review articles where virtually no experimental details were provided. We have used this method to prepare $Li_3CoF_6$, $Na_3CoF_6$ and $K_3CoF_6$ from the corresponding $M_3Co(CN)_6$ salts. In addition, $Ba_3(CoF_6)_2$ has been prepared from $Ba_3[Co(CN)_6]_2$ and $K_2NaCoF_6$ from a substance of empirical composition $K_2NaCo(CN)_6$. While we shall present evidence that $K_2NaCoF_6$ is a true compound, we do not know for certain whether the starting material is a compound or a mixture of $K_3Co(CN)_6$ and $Na_3Co(CN)_6$. Experimental details of the preparations and analyses are summarized in Table I.

An attempt to prepare $La[CoF_6]$ by fluorination of $LaCo(CN)_6$ failed. The evidence indicates that we obtained $LaF_3 + CoF_3$ instead. It seems reasonable to explain this on the basis of lattice energy differences; that is, we assume that the sum of the lattice energies of $CoF_3$ and $LaF_3$ exceeds the lattice energy of $La[CoF_6]$ (ignoring entropy differences which are unlikely to be large). Since $La^{+3}$ has a very high charge-to-radius ratio, the occurrence of phase separation in this system but not in many others with cations of smaller charge-to-radius ratio appears reasonable.

**X-Ray Studies.**—X-Ray powder studies have been made of all compounds prepared. Hoppe[6] and Klemm[7] have stated that $Na_3CoF_6$ and $K_3CoF_6$ are cubic with unit cell edges, $a_0$, of 8.13 and 8.55 Å., respectively, at room temperature. They also state that the compounds were isomorphous with $K_3FeF_6$.[8] Structures of this general type[9] are derived from the cubic $CaF_2$ (fluorite) structure. In $K_2SiF_6$,[10] $K^+$ ions occupy the $F^-$ sites of $CaF_2$ while $[SiF_6]^{-2}$ ions occupy the $Ca^{+2}$ positions of $CaF_2$. This arrangement produces a cubic unit cell with complex ions at each corner and at each face center. The $K^+$ ions occupy the centers of the eight quadrants of the unit cube. To increase the number of cations per formula unit to three, as in $K_3MF_6$, a potassium ion is placed at the center of the unit cell

---

[1] It also occurs in Co(III) ions in certain oxide systems but these are not suited to the objectives of our work.

[2] F. A. Cotton and M. D. Meyers, THIS JOURNAL, **82**, 5023 (1960).

[3] R. L. Mitchell, Thesis, University of Buffalo, 1938.

[4] B. Cox and A. G. Sharpe, *J. Chem. Soc.*, 1798 (1954).

[5] W. Klemm and E. Huss, *Z. anorg. u. allgem. Chem.*, **258**, 221 (1949).

[6] R. Hoppe, *Rec. trav. chem.*, **75**, 569 (1956).

[7] W. Klemm, *Bull. soc. chim. France*, 1323 (1956).

[8] L. Pauling, THIS JOURNAL, **46**, 2738 (1924).

[9] R. W. G. Wyckoff, "Crystal Structures," Vol. III, Interscience Publishers, Inc., New York, N. Y., 1953, Chap. IX, text page 27.

[10] A. F. Wells, "Structural Inorganic Chemistry," Oxford Press, London, 1945, p. 289.

TABLE I

PREPARATIVE DETAILS AND ANALYSES OF $[CoF_6]^{-3}$ SALTS

| Run no. | Starting material | | Fluorination | | Weight loss | | Analyses, % | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | Calcd. | | | | | Found[a] | | | |
| | Formula | Weight, g. | Temp., °C. | Time, hr. | Calcd. | Found | Compound | K | Ba | Co | F | K | Ba | Co | F |
| 1 | $K_3Co(CN)_6$ | 9.554 | 300–330 | 7 | 1.216 | 1.167 | $K_3CoF_6$ | 40.41 | . . . | 20.31 | 39.28 | 39.53 (2) | . . . | 20.22 (4) | 39.00 (2) |
| 2 | $K_3Co(CN)_6$ | 4.582 | 330–340 | 6.5 | 0.581 | 0.546 | $K_3CoF_6$ | 40.41 | . . . | 20.31 | 39.28 | 40.75 (2) | . . . | 20.08 (4) | 38.20 (4) |
| 3 | $Ba_3[Co(CN)_6]_2 \cdot H_2O$ | 0.625 | 285–310 | 3.5 | .075 | .074 | $Ba_3(CoF_6)_2$ | . . . | 54.37 | 15.55 | 30.08 | . . . . . . | 54.53 | 15.0 | 30.65 |
| 4 | $Ba_3[Co(CN)_6]_2 \cdot 1.7H_2O$ | 3.019 | 290–310 | 7 | .397 | .360 | $Ba_3(CoF_6)_2$ | . . . | 54.37 | 15.55 | 30.08 | . . . . . . | 55.08 | 15.19 | 30.41 |
| 5 | $Ba_3[Co(CN)_6]_2 \cdot 1.4H_2O$ | 3.290 | 260–290 | 7 | .415 | .389 | $Ba_3(CoF_6)_2$ | . . . | 54.37 | 15.55 | 30.08 | . . . . . . | 53.03 | 14.91 | 29.54 |
| 6 | $Na_3Co(CN)_6$ | 2.261 | 320–340 | 8 | .336 | .310 | $Na_3CoF_6$ | . . . | . . . | 24.36 | 47.12 | . . . . . . | . . . | 21.86 | 48.21 |
| | $Na_3Co(CN)_6$ | 2.261 | 320–340 | +3 = 11 | .336 | .314 | | | | | | . . . . . . | . . . | 20.90 | 42.66 |
| 7 | $K_2NaCo(CN)_6$ | 1.20 | 330–350 | 4 | .160 | .146 | $K_2NaCoF_6$ | . . . | . . . | 21.50 | 41.59 | . . . . . . | . . . | 28.21 | 59.38 |
| 8 | $Li_3Co(CN)_2 \cdot 2H_2O$ | 1.927 | 320–340 | 5 | .552 | .537 | $Li_3CoF_6$ | . . . | . . . | 30.42 | 58.83 | | | | |

[a] Numbers in parentheses indicate number of replicate determinations.

and twelve others are placed at the mid-points of each unit cube edge.

The discussion of our X-ray data will be based upon analogies with the data for $M_3AlF_6$ and similar systems and especially with the results of Steward and Rooksby.[11] These workers established that there is a general pattern of behavior in compounds of this class. All of them are cubic (space group Fm3m–$O_h^5$) at a sufficiently high temperature. On cooling, the lattice contracts until at a temperature characteristic of each substance, distortion sets in. For $Na_3AlF_6$ (cryolite, either natural or synthetic) the structure is cubic above 550° but becomes distorted to monoclinic, increasingly so as the temperature falls, below 550°. With $K_3AlF_6$ the critical temperature is below 300°; the lattice is tetragonal, with $a_0$ = 8.40 and $c_0$ = 8.46 at 20°. This distortion is manifested as very slight line splittings in the powder picture. $(NH_4)_3FeF_6$ and $(NH_4)_3AlF_6$ were found to be cubic at 20° but tetragonally distorted at −180°. $K_2NaAlF_6$ was found to be cubic at 20° and still cubic at −180°. The stability of the cubic structure of $K_2NaAlF_6$ in a temperature range where both $K_3AlF_6$ and $Na_3AlF_6$ are distorted was attributed by Steward and Rooksby to the placement of the K ions at the centers of the octants and the Na ions at the other cation sites, sites of these two sorts occurring in a 2:1 ratio. This proposal of site occupancy had been substantiated by Manzer.[12]

Our powder pictures of $K_3CoF_6$ confirm the conclusion of Klemm and Hoppe. All lines present have $h + k$, $h + l$ and $k + l$ even, as required by a face-centered lattice and all lines can be satisfactorily indexed assuming the cubic structure described above with $a_0$ = 8.55 Å. at ~ 25°. We should like to note, however, that small distortions of 0.01–0.1 Å. to give perhaps a tetragonal unit cell probably would escape detection. Since refined work[13] on $K_3AlF_6$ has revealed a slight tetragonal distortion ($c_0 - a_0 \approx 0.06$ Å.) at 20° it would not be unlikely that a similar distortion might occur at room temperature in $K_3CoF_6$ where the $MF_6$ octahedrals are somewhat larger.

Considering that $Na_3AlF_6$ has a greater tendency to distortion than does $K_3AlF_6$, Klemm and Hoppe's report that $Na_3CoF_6$ is cubic at room temperature seemed surprising. We find that the powder pictures of $Na_3CoF_6$ and $Na_3AlF_6$ at room temperatures show considerable resemblance, although intensities vary as would be expected. This suggests that there may be a monoclinic distortion of $Na_3CoF_6$ similar to that in $Na_3AlF_6$. At the very least it may be said that the pattern for $Na_3CoF_6$ definitely indicates distortion of some kind for it is more complex than those for $K_3CoF_6$, $K_3FeF_6$ or $K_3AlF_6$.

$K_2NaCoF_6$ was found to have the d-spacings given in Table II. These results indicate that $K_2NaCoF_6$ like $K_2NaAlF_6$ is truly cubic at room temperature. Moreover, the powder picture clearly shows that $K_2NaCoF_6$ is a true compound and not a mixture of $K_3CoF_6$ with $Na_3CoF_6$.

---

[11] E. G. Steward and H. P. Rooksby, *Acta Cryst.*, **6**, 49 (1953).

[12] G. Manzer, *Fortschr. Mineral.*, **17**, 61 (1932).

[13] C. Brosset, *Ark. Kemi, Mineral. Geol.*, **21A**, No. 9 (1946).

TABLE II

D-SPACINGS FOR $K_2NaCoF_6$

| Index (*hkl*) | Calcd.[a] | Found[b] |
|---|---|---|
| 111 | 4.74 | 4.73 w |
| 200 | 4.11 | 4.09 vvw |
| .. | .. | 3.81 vw[c] |
| .. | .. | 3.44 vvw[c] |
| 220 | 2.91 | 2.91 vs |
| 311 | 2.48 | 2.48 vvw |
| 222 | 2.37 | 2.37 m |
| 400 | 2.06 | 2.06 vs. |
| 422 | 1.68 | 1.68 ms |
| 511, 333 | 1.58 | 1.59 vvw |
| 440 | 1.45 | 1.46 ms |
| 620 | 1.30 | 1.31 w |
| 444 | 1.19 | 1.19 w |

[a] Calculated for cubic structure using $a = 8.22$ Å. [b] w = weak, s = strong, m = medium, v = very. [c] These lines cannot be indexed and are believed due to impurities, although they do not correspond to any of the three strongest lines of $CoF_3$, NaF, KF, CoO or $Co_2O_3$, 3.81 may be due to $Na_3CoF_6$ where it occurs strongly.

No satisfactory powder photograph was obtained for $Ba_3(CoF_6)_2$ in several attempts. The sample in the capillary tube was dark after the X-ray exposure. A few strong lines, in addition to many weak and diffuse lines, were observed, suggestive of decomposition and/or a unit cell of low symmetry. A powder photograph of $Li_3CoF_6$ which had not been pulverized showed only discrete spots. Grinding the sample caused decomposition within about 10 minutes.

**Infrared Spectra.**—Until the recent work of Peacock and Sharp[14] (who cite the limited earlier literature) little attention had been given to the infrared spectra and Raman spectra of salts containing $MF_6$ anions, although there has been considerable study of gaseous, neutral hexafluorides.[15] $MF_6$ species will, in the absence of distortions of a regular octahedral structure, belong to the point group $O_h$ and have therefore only two infrared-active fundamental modes of vibration. One (usually designated $\nu_3$) is principally an M–F stretching motion, and the other ($\nu_4$) is mainly an F–M–F angle bending motion. Peacock and Sharp studied the variation in the frequencies of these modes, especially $\nu_3$, as a function of the metal atom M and the charge, but there has not been any systematic study of the effect of changing crystal environment upon the spectrum of one anion. We have examined the effects of environment upon both $\nu_3$ and $\nu_4$ in the anions $AlF_6^{-3}$ and $CoF_6^{-3}$. The main results are presented in Table III. It will be observed that the positions of the bands are essentially insensitive to the lattice in which the $AlF_6^{-3}$ and $CoF_6^{-3}$ anions find themselves. There are, however, significant variations in the widths of the bands which appear to be related in a qualitative way to the existence of or degree of departure from strict octahedral site symmetry in the various lattices.

The spectrum of $K_2SiF_6$ is given for comparison since it has been found[16,17] that the $SiF_6^{-2}$ octahedra are perfectly regular in this compound and so oriented that their site symmetry is $O_h$. Recent studies have confirmed these results at and below room temperature.[18] Hence the very symmetrical envelopes and small widths of the bands for this substance may be considered representative of what can be expected for a completely symmetrical $MF_6$ anion. In agreement with this hypothesis, the bands of $AlF_6^{-3}$ in $K_2NaAlF_6$, already known to have a strictly cubic structure, are similarly symmetrical and narrow. The very close similarity of the bands in $K_2NaCoF_6$ to those in $K_2NaAlF_6$ and $K_2SiF_6$ then provides excellent confirmation for the conclusion, reached above on the basis of the X-ray data, that $K_2NaCoF_2$ is strictly cubic with undistorted $CoF_6^{3-}$ octahedra.

It also will be seen that in the sodium and potassium salts of $AlF_6^{-3}$ and $CoF_6^{-3}$, for which X-ray data indicate some departure from perfect cubic symmetry of the lattice, the widths of $\nu_3$ are significantly greater than in the perfectly cubic lattices. Since the X-ray data suggest that *lattice* distortion is greater in the sodium salts than in the potassium salts, it might have been anticipated that the band widths would be greater for the sodium than for the potassium salts. As Table III shows, the band widths differ by an amount scarcely outside of experimental error but apparently in the opposite sense. If this inverse variation is real, it is not necessarily enigmatic, for it is possible to imagine that the slightly more distorted *lattice* might nevertheless contain the slightly less distorted $MF_6$ *octahedra.*

For $Li_3CoF_6$, where the lattice is known to be far from cubic, there is a pronounced broadening of both bands, especially $\nu_3$, and for $Ba_3[CoF_6]_2$ which is also not cubic it appears that there is actually a splitting of $\nu_3$ into two bands.

Thus taken qualitatively, the infrared spectra corroborate the conclusions previously reached as to the varying degrees of distortion of the $MF_6$ octahedra in the compounds examined.

## Experimental

**Preparation of $Co(CN)_6^{-3}$ Salts.**—Anhydrous $K_3Co(CN)_6$ was prepared according to Bigelow.[19] For the preparation of the other salts, $H_3Co(CN)_6 \cdot xH_2O$ was required. This was prepared by precipitating $Ag_3Co(CN)_6$, a slurry of which was then treated with $H_2S$. The $Ag_2S$ was filtered off and the clear yellow filtrate evaporated in vacuum to a white residue. Continued pumping of this residue for 24 hr. at 60–70° gave a white product with sternutatory properties. Determination of acid equivalents and elemental analyses (Co, N) showed that the products so obtained in various preparations were $H_3CO(CN)_6 \cdot xH_2O$ with $x$ varying from 0.3 to 0.5.

**$Ba_3[Co(CN)_6]_2 \cdot H_2O$.**—This substance has been mentioned in the literature before but in highly hydrated form.[20,21] We desired as anhydrous a product as possible. $H_3Co(CN)_6 \cdot 0.3H_2O$ in water was carefully neutralized with a stoichiometric quantity of $Ba(OH)_2 \cdot 8H_2O$. Upon or shortly before the addition of all of the $Ba(OH)_2 \cdot 8H_2O$, the *p*H reached a value of 6.0 and the solution became slightly cloudy (probably $BaCO_3$). After filtering, the clear, light yellow solution was evaporated in vacuum. Crystals of the

---

(14) R. D. Peacock and D. W. A. Sharp, *J. Chem. Soc.*, 2762 (1959).

(15) See ref. 14 for literature citations.

(16) J. A. Ketelaar, *Z. Krist.*, **92**, 155 (1935).

(17) R. M. Bozorth, THIS JOURNAL, **44**, 1066 (1922).

(18) R. C. L. Slater, Dept. of Physics, M.I.T., personal communication.

(19) J. H. Bigelow, "Inorganic Syntheses," Vol. II, McGraw-Hill Book Co., New York, N. Y., 1946, p. 225.

(20) A. Ferrari and L. Coghi, *Gazz. chim. ital.*, **69**, 3 (1939).

(21) R. W. G. Wyckoff, "Crystal Structures," Vol. III, Interscience Publishers, Inc., New York, N. Y., 1953, Chap. IX, text page 27.

TABLE III

NUMERICAL PARAMETERS OF INFRARED SPECTRA OF $SiF_6^{-2}$, $AlF_6^{-3}$ AND $CoF_6^{-3}$ SALTS

| | $\nu_3$ | | $\nu_4$ | | |
|---|---|---|---|---|---|
| Compound | Max., cm.$^{-1}$ | Width at $^1/_2$ ht., cm.$^{-1}$ | Max. cm.$^{-1}$ | Width at $^1/_2$ ht., cm.$^{-1}$ | Crystal structure at 25° |
| $K_2SiF_6$ | 753 | 75 ± 5 | 485 ± 5 | 13 ± 2 | Cubic |
| $K_2NaAlF_6$ | 600 ± 10 | 90 ± 20 | 405 ± 5 | 17 ± 2 | Cubic |
| $K_2NaCoF_6$ | 510 ± 10 | 75 ± 10 | 310 ± 5 | 25 ± 5 | Cubic |
| $K_3AlF_6$ | 595 ± 10 | 130 ± 10 | 392 ± 5 | 32 ± 5 | Slight tetrag. |
| $K_3CoF_6$ | 475$^a$ | 140 ± 15 | 310 ± 10 | 25 ± 10 | Slight tetrag. |
| $Na_3AlF_6$ | 600 ± 15 | 100 ± 10 | (416, 400) ± 5$^b$ | 40 ± 10$^b$ | Monoclinic |
| $Na_3CoF_6$ | 500 ± 10 | 110 ± 30 | (340(sh), 320) ± 5$^b$ | 35 ± 10$^b$ | Monoclinic |
| $Ba_3[CoF_6]_2$ | 480 ± 10$^c$ | ~150 | 320 ± 5 | 40 ± 10 | Unknown, not cubic |
| $Li_3CoF_6$ | ~500 | Very broad$^d$ | Not observed | | Unknown, not cubic |

[a] There is considerable uncertainty in locating "the" band maximum, submaxima which are always very poorly resolved but apparently reproducible appear at ~505, ~480 and ~450 cm.$^{-1}$. [b] $\nu_4$ is often broad on the high frequency side, but in these compounds a second band is clearly discernible; the "width" is the combined widths of both bands. [c] There is also a weaker band at ~620 cm.$^{-1}$ with some absorption between it and the main band at ~480 cm.$^{-1}$. [d] The adsorption begins at about 700 cm.$^{-1}$ and has a value of 50% at 400 cm.$^{-1}$; the width is >300 cm.

product began to appear when the concentration reached 0.3-0.4 molar. Evaporation under vacuum then was continued to dryness while maintaining the solution at 60-70°. The solid was further dried under vacuum over $P_2O_5$ in a drying pistol at 140° for 24 hr.

*Anal.* Calcd. for $Ba_3[Co(CN)_6]_2$: Ba, 48.9; for $Ba_3[Co(CN)_6]_2 \cdot H_2O$: Ba, 47.9. Found: Ba, 47.8 (1st batch), 47.6 (2nd batch).

$Na_3Co(CN)_6$ was prepared by neutralizing $H_3Co(CN)_6$ with the stoichiometric quantity of $Na_2CO_3$ (*p*H 7). Filtration and evaporation followed by drying overnight at 145° in vacuum afforded the anhydrous compound. $K_2NaCO(CN)_6$ was prepared by mixing solutions containing $Na_3Co(CN)_6$ and $K_3Co(CN)_6$ in 1:2 mole ratio, evaporating to dryness and drying in vacuum 24 hr. at 70°. On the basis of yield (103%) calculated as anhydrous $K_2NaCo(CN)_6$ it was concluded that the product was essentially anhydrous.

$Li_3Co(CN)_6$ was prepared by evaporation of a solution prepared by mixing stoichiometric amounts of $H_3Co(CN)_6$ and LiOH, evaporating to dryness and drying in vacuum at 140°. This material doubtless was a hydrate, but by this point in the work it had been concluded that use of anhydrous cobalt cyanides probably was not essential and it was therefore used without further drying.

**Preparation of $[CoF_6]^{-3}$ Salts.**—The fluorination apparatus used was very similar to that described in detail by Priest.[22] Fluorine was purchased from the Pennsalt Chemical Co. and used without further purification. The elevated temperatures required for the fluorinations were provided by a tubular furnace and the temperatures were measured by a thermocouple junction in a well placed within a centimeter of the nickel boats containing the samples.

The general procedure was the same for all compounds. A weighed quantity of the appropriate $[Co(CN)_6]^{-3}$ salt in a weighed Ni boat was placed in the apparatus which usually was preheated to ~100°. The apparatus then was swept for 1-2 hr. with dry nitrogen. Sweeping with fluorine was then begun and continued throughout the run at a rate of about 30 cc. per min. After ~0.5 hr. of sweeping with fluorine the temperature was quickly raised to operating temperature. After fluorination was complete the oven was cooled while displacing the fluorine with nitrogen. The boats were removed from the nitrogen atmosphere at temperatures of 100-150° and immediately placed in a vacuum desiccator over $P_2O_5$. When the sample was completely cool it was weighed quickly. Specific details for each run are given in Table I. We attempted the preparation of $La[CoF_6]$. Anhydrous $LaCo(CN)_6$, made by heating $LaCo(CN)_6 \cdot 9/2H_2O$[23] in a vacuum at 140° for 12 hr., was fluorinated for 6 hr. at 300-330°. The product was light brown in color indicating the presence of $CoF_3$. An X-ray powder picture definitely showed the presence of $LaF_3$. Fluorination to $CoF_3 + LaF_3$ was shown to be complete by analysis (calcd.: F, 36.55; found: 36.70).

$K_3AlF_6$ was prepared by the method of Paine and Pearson.[24] An X-ray powder photograph of the product showed the nine strongest lines reported in the ASTM index[25] for $K_3AlF_6$. Two very weak lines due to KF also were found. $K_2NaAlF_6$ was prepared by dissolving the correct amount of aluminum metal in a solution containing KOH and NaOH in 2:1 mole ratio. The solution was then neutralized with aqueous HF and evaporated to dryness. An X-ray powder diffraction pattern confirmed the identity of the material.[25]

The sample of $K_2SiF_6$ was quite pure material prepared for X-ray work and kindly given to us by Dr. R. C. L. Slater.

**Analytical Methods.**—Fluorine was separated by volatilization[26] from concd. $HClO_4$ in a glass apparatus. Samples of ~100 mg. were used with 80-100 ml. of distillate being collected. The fluoride was weighed as PbClF.[27] Trial runs on known substances, *e.g.*, cryolite of 99.99% purity (kindly given by the Pennsalt Co.) indicated that we would obtain results correct to within ~0.2% (low). Cobalt was determined by EDTA titration.[28] Calibration runs indicated results should be reliable to within ±0.3%. Potassium was precipitated with sodium tetraphenylboron[29]; test runs indicated our results should be accurate to within ±0.5%. Barium was precipitated as sulfate in the standard way.

**X-Ray Studies.**—X-Ray powder diffraction patterns of the hexafluorocobaltates were obtained on photographic film with a General Electric XRD3 X-ray diffraction unit and a North American Phillips powder camera of 57.3 mm. radius. Samples were loaded into 0.3 mm. diameter Pyrex capillaries and irradiated with CuK$\alpha$ radiation using a nickel filter. The pictures were indexed in the standard manner,[30] and a film shrinkage correction, applied to each arc length measured, was obtained from an NaCl calibration pattern.

**Infrared Spectra.**—These were obtained using a Baird Infrared Recording Spectrophotometer, Model AB2, fitted with a KBr prism and a Beckman Model IR4 fitted with a CsBr prism. Calibrations were made with the 12.38 $\mu$ band of ammonia. Substantially identical spectra were obtained with both Nujol mulls and freshly prepared KBr and KI pressings of the compounds.

**Acknowledgments.**—We gratefully acknowledge financial support in the form of the Procter and Gamble Fellowship 1957-1958 and a Summer NSF Fellowship to M. D. M. and from the U. S. Atomic Energy Commission under Contract No. AT(30-1)-1965.

---

(22) H. F. Priest, "Inorganic Syntheses," Vol. III, McGraw-Hill Book Co., New York, N. Y., 1950, p. 174.

(23) C. James and P. S. Willand, THIS JOURNAL, **38**, 1497 (1916).

(24) F. A. Paine and J. Pearson, *J. Chem. Soc.*, 1172 (1947).

(25) American Society for Testing Materials, *Data Cards* for the Identification of Crystalline Materials.

(26) H. H. Willard and O. B. Winter, *Ind. and Eng. Chem., Anal. Ed.*, **5**, 7 (1933).

(27) W. F. Hillebrand and G. E. F. Lundell, "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 744.

(28) F. J. Welcher, "The Analytical Uses of Ethylenediamine Tetraacetic Acid," D. Van Nostrand Co., Princeton, N. J., 1958, p. 230.

(29) G. H. Gloss, *Chemist Analyst*, **42**, 50 (1953).

(30) L. A. Azaroff and M. J. Buerger, "The Powder Method," McGraw-Hill Book Co., New York, N. Y., 1958, Chap. 7.