the remaining viscous liquid was triturated with 400 ml of petroleum ether (bp 30–60°) to give 7.2 g of solid product which was recrystallized from ethylene dichloride; mp 138–143°. *Anal.* Calcd for $C_{16}H_{50}B_{50}Cl_2O_6$: C, 20.22; H, 5.30; B, 56.92; Cl, 7.46; mol wt, 950.5. Found: C, 19.56; H, 5.34; B, 56.28; Cl, 7.19; mol wt (in chloroform), 971.

From the above filtrate the petroleum ether was evaporated and the remainder subjected to vacuum distillation. The highly viscous distillation residue (8 g) was free of volatile products and not further purified. *Anal.* Calcd for $C_{10}H_{30}B_{30}Cl_2O_4$: C, 19.69; H, 4.96; B, 53.22; Cl, 11.63; mol wt, 609.9. Found: C, 20.84; H, 5.33; B, 51.08; Cl, 11.60; mol wt (in benzene), 586. The yield of distillate [m-$B_{10}H_{10}C_2(CO\cdot Cl)_2$] was 9.7 g (20%); bp 67° (0.1 mm); n^{26}D 1.5443.

m-$B_{10}H_{10}C_2(CO\cdot NH_2)_2$.—Ammonia was passed through a benzene solution of m-$B_{10}H_{10}C_2(CO\cdot Cl)_2$ to give the corresponding diamide in quantitative yield; mp (after recrystallization from xylene) 183° (lit.[5] 184–185.5°).

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Preparation, Single Crystal Growth, and Crystallographic Properties of FeF_2, $RbFeF_3$, and $CsFeF_3$

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This note is concerned with the preparation, single crystal growth, and crystallographic properties of $RbFeF_3$ and $CsFeF_3$ and with the single crystal growth of FeF_2. The crystal structure of FeF_2 was reported by Stout and Reed to be of the rutile type.[1] Recently, Baur[2] redetermined the atomic parameters of FeF_2 and found that two of the Fe–F distances were more than 6% shorter than the other four in the FeF_6 octahedra. The existence of $RbFeF_3$ and $CsFeF_3$ has not been reported previously. The magnetic properties of $RbFeF_3$ have been measured by Wang and Kestigian.[3]

Experimental Section

Single crystals of FeF_2 were prepared by sublimation. Either $FeF_2\cdot xH_2O$ or C + Fe_2O_3 was heated to 950–1000° in an HF–Ar carrier gas transport system. The temperature was maintained for 2 to 3 days. Long, colorless, transparent needles, typically 2 cm in length × 2 mm in cross section, were deposited in the cooler regions of the furnace.

Single crystals of $RbFeF_3$ and $CsFeF_3$ were obtained by the horizontal Bridgman and/or temperature gradient techniques. Equimolar mixtures of the respective anhydrous fluorides were intimately mixed and heated in dense graphite containers. An HF–Ar atmosphere was used to protect the sample during the crystal growth procedure. Colorless, transparent single crystals of 2 in. × 0.5 in. dimensions were usually obtained.

Analysis.—Samples were weighed and dissolved in dilute HCl. The ferrous content was determined as follows. Sulfuric acid was added and the sample heated to fuming to expel all of the fluorine. After dilution, the solution was passed through a Jones reductor and titrated with standardized dichromate solution.

Anal. Calcd for FeF_2: Fe, 59.51. Found: Fe, 58.68.
Anal. Calcd for $RbFeF_3$: Fe, 28.16. Found: Fe, 28.08.
Anal. Calcd for $CsFeF_3$: Fe, 22.72. Found: Fe, 22.55.

The rubidium, cesium, and fluoride contents were calculated by difference. The iron present in the samples was determined to be divalent. The concentration of trivalent iron in the crystals was found to be 10 ppm (or less). Spectrographic analysis of ferrous fluoride single crystals revealed the presence of trace amounts (1–10 ppm range) of copper, silicon, nickel, cobalt, manganese, chromium, and aluminum as the total impurities.

Crystallography

The values of the crystallographic cell constants for FeF_2 reported by Baur[2] were essentially confirmed.

Anhydrous $RbFeF_3$ was found to possess the ideal (cubic) perovskite structure with a = 4.174 A. The data reported in Table I were taken with a high angle diffractometer using a curved crystal monochromator and a scintillation counter detector. Copper radiation was used.

TABLE I

X-RAY DATA FOR $RbFeF_3$

hkl	d_{calcd}	d_{obsd}	I/I_0	hkl	d_{calcd}	d_{obsd}	I/I_0
110	2.95	2.94	10.0	321	1.115	1.115	0.6
111	2.41	2.40	1.5	400	1.0435	1.0433	0.2
200	2.086	2.081	5.0	410	1.012	1.0125	<0.1
211	1.704	1.700	2.4	411–330	0.9837	0.9834	1.3
220	1.475	1.473	1.9	331	0.9573	0.9577	0.1
310	1.320	1.319	1.0	420	0.9331	0.9332	0.3
311	1.258	1.258	0.2	332	0.8899	0.8899	0.1
222	1.205	1.204	0.3				

Prolonged exposure did not reveal the presence of any extraneous weak lines or line splitting indicative of slight distortions of the cubic lattice. The density of $RbFeF_3$ was determined experimentally to be 4.53 at 21° as compared with the theoretical density of 4.54. The optically isotropic single crystals were found by the immersion method to have a refractive index of 1.508. The compound melts congruently at 880 ± 5° as indicated by its sharpness of melting on a hot stage microscope. Although precautions were taken to prevent oxidation of the sample by flushing the microscope heating chamber with helium that had passed through a trap cooled with liquid nitrogen, the transparent crystals discolored upon melting.

Cesium ferrous trifluoride ($CsFeF_3$) exhibits hexagonal symmetry caused by a slight distortion along a threefold axis of the ideal perovskite structure. The unit cell parameters were found to be a = 6.158 A and c = 14.855 A. The c dimension derived from the cubic unit cell had to be doubled to index weak X-ray reflections that are observed. X-Ray data for $CsFeF_3$ are presented in Table II. The density of $CsFeF_3$ was 4.94 as measured in toluene at 21°. The calculated density assuming six molecules of $CsFeF_3$ per unit cell is 5.02.

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(1) J. W. Stout and S. A. Reed, *J. Am. Chem. Soc.*, **76**, 5279 (1954).

(2) W. H. Baur, *Acta Cryst.*, **11**, 488 (1958).

(3) F. F. Y. Wang and M. Kestigian, presentation, American Physical Society, Nov 1965, San Francisco, Calif.

TABLE II

X-RAY DATA FOR $CsFeF_3$

hkl	d_{calcd}	d_{obsd}	I/I_0	hkl	d_{calcd}	d_{obsd}	I/I_0
103	3.628	3.62	5.3	214	1.772	1.772	4.9
110	3.079	3.07	10.0	215	1.668	1.668	0.4
104	3.044	3.05	6.3	207	1.661	1.660	0.8
021	2.625	2.624	0.6	118	1.590	1.590	0.6
105	2.595	2.592	0.4	109	1.577	1.577	0.6
202	2.509	2.506	1.6	220	1.540	1.539	1.8
006	2.475	2.473	1.4	208	1.524	1.524	0.6
203	2.347	2.347	4.9	217	1.463	1.462	0.6
204	2.166	2.164	6.5	313	1.417	1.418	0.6
205	1.984	1.984	1.0	209	1.403	1.403	0.6
107	1.972	1.971	1.0	314	1.374	1.374	1.8
116	1.930	1.929	0.6	226	1.307	1.307	0.6
213	1.867	1.867	0.8	403	1.287	1.287	0.3
300	1.778	1.777	3.1	404	1.255	1.256	0.7

The melting point of $CsFeF_3$ was found to be 708 ± 5°. The transparent crystals are uniaxial positive with $n_\omega = 1.544$ and $n_\epsilon = 1.560$.

Summary

Single crystals of FeF_2, $RbFeF_3$, and $CsFeF_3$ were successfully prepared. X-Ray diffraction data obtained at room temperature indicate $RbFeF_3$ to possess the cubic perovskite structure with $a = 4.174$ A and $CsFeF_3$ to exhibit a hexagonal distortion of the ideal perovskite structure with $a = 6.158$ A and $c = 14.855$ A. The distortion from cubic symmetry involves a shortening of one (111) direction which becomes one-half the c axis of the hexagonal unit cell.

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The Reaction of Cyclopolyphosphines with Boron Halides[1]

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The behavior of cyclopolyphosphines toward transition metal compounds has received some attention recently.[2] However, very little has been published concerning the reactivity of cyclopolyphosphines toward Lewis acids such as the boron halides. Mahler and Burg[3] report that $(CF_3P)_4$ is not attacked by BF_3, B_2H_6, or protic acids within reasonable temperature limits, whereas Kuchen and Buchwald[4] were able to isolate a material of empirical composition $(C_6H_5P)_3\cdot BF_3$ from the reaction of form A of $(C_6H_5P)_n$ (n has been shown to be 5 for this form[5]) with BF_3 in benzene solution. The objects of the present work were (a) to see if Kuchen and Buchwald's interesting observations could be repeated and (b) to extend the scope of the reaction to include other boron halides and other cyclopolyphosphines.

Experimental Section

Reagents.—The boron halides were obtained from commercial sources and were used without further purification. Form A of $(C_6H_5P)_n$ was prepared by the magnesium coupling of $C_6H_5PCl_2$ following the directions of Henderson, *et al.*[6] Tetra-*n*-butylcyclotetraphosphine was prepared by Rauhut and Semsel's method.[7] We found that the ethyl and *n*-propyl homologs could also be prepared in comparable yields by the same method.

General Procedure.—The BF_3 and BCl_3 compounds were prepared by bubbling BF_3 or BCl_3 through a benzene or *n*-hexane solution of the cyclopolyphosphine [at 0° in the case of $(C_6H_5P)_n$]. The BBr_3 compounds were prepared by adding a slight excess of BBr_3 (diluted with solvent) to a benzene or *n*-hexane solution of the cyclopolyphosphine. In each case the product was isolated by vacuum evaporation of the solvent plus excess boron halide. Generally, this left oily materials which slowly solidified upon standing under a nitrogen atmosphere. Several days was required for the solidification of compounds IV through XII. With the exception of I and II the compounds gradually softened over a wide range of temperatures. Compound I melted at 130–140° and compound II at 185–195°. No suitable recrystallization solvents were discovered. The analytical data are presented in Table I.

All operations were carried out under a dry nitrogen atmosphere owing to the ease of hydrolysis and/or oxidation of both products and starting materials.

Spectra.—The infrared spectra of Nujol mulls or liquid films were run on a Beckman IR 7 spectrophotometer equipped with NaCl and CsI optics. Oxidation of the mulls or films was prevented by the insertion of thin Teflon gaskets between the NaCl or CsI plates.

Discussion

Like Kuchen and Buchwald[4] we have been able to isolate a compound of empirical composition $(C_6H_5P)_3\cdot BF_3$ from the reaction of form A of $(C_6H_5P)_n$ with BF_3. The observed stoichiometry would imply an equation such as[8]

$$3(C_6H_5P)_4 + 4BF_3 \longrightarrow 4(C_6H_5P)_3\cdot BF_3$$

It is also evident that other boron halides will react with the same cyclopolyphosphine to give the analogous products II and III. The fact that two BBr_3 molecules react per three C_6H_5P units (compound III) probably relates to the higher acid strength of BBr_3. Products of empirical composition $(RP)_2\cdot BX_3$ are obtained from the reaction of alkyl-substituted cyclopolyphosphines with

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[1] Presented in part at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965.

[2] A. B. Burg and W. Mahler, *J. Am. Chem. Soc.*, **80**, 2334 (1958); K. Issleib and W. Seidel, *Z. Anorg. Allgem. Chem.*, **303**, 155 (1960); H. G. Ang and J. S. Shannon, *Chem. Commun.*, 10 (1965); G. W. A. Fowles and D. K. Jenkins, *ibid.*, 61 (1965); D. G. Hicks and J. A. Dean, *ibid.*, 172 (1965).

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[4] W. Kuchen and H. Buchwald, *Chem. Ber.*, **91**, 2296 (1958).

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[6] W. A. Henderson, M. Epstein, and F. S. Seichter, *J. Am. Chem. Soc.*, **85**, 2462 (1963).

[7] M. M. Rauhut and A. M. Semsel, *J. Org. Chem.*, **28**, 473 (1963).

[8] Although form A of $(C_6H_5P)_n$ has recently been shown to be $(C_6H_5P)_5$ in the solid phase (ref 5), we have written the equation in terms of $(C_6H_5P)_4$ because this appears to be the molecular form in solution. See W. A. Henderson, M. Epstein, and F. S. Seichter, *J. Am. Chem. Soc.*, **85**, 2462 (1963); W. Kuchen and H. Buchwald, *Chem. Ber.*, **91**, 2296 (1958); and F. Pass and H. Schindlbaur, *Monatsh.*, **90**, 148 (1959).