the limit of observation) but there are significant differences for the reflections 03.1 and 02.3. These discrepancies probably are due to inadequacy of the atomic coordinates used in calculating structure factors; no attempt has been made to refine the coordinates because of the small number of $|F_{\text{obsd}}|$ values available.

The crystal chemistry of phases related to Fe_7C_3 has recently been discussed.[9b,15]

Experimental

Diffractometer Measurements.—The sample used was obtained from Dr. J. D. Louw[5] (S.A. Coal, Oil and Gas Corporation, Sasolburg, South Africa). The present X-ray measurements were made using a Philips PW 1010 highly-stabilized X-ray generator, a PW 1050 diffractometer, and associated counting equipment. The argon-filled Geiger counter used was linear to about 400 c.p.s. and this counting rate was not exceeded. Co Kα radiation (Fe filter, 36 kv., 10 ma.) was used; the specimen was contained in a PW 1064 specimen spinner; the angular velocity of the counter was 1/8° 2θ per minute. Integrated intensities were obtained by planimeter integration of chart records. The intensity measurements covered a period of 3 days and suitable checks were made on standard peaks to ensure that no drift in the apparatus had occurred during this time.

A portion of the diffraction pattern is shown in Fig. 1. The impurities detected were Fe_3O_4, Hägg carbide (Fe_5C_2), and an unknown material giving a diffraction peak at $2\theta = 47.30°$ ($d = 2.230$ Å.). All the other reflections could be indexed in terms of the $D10_2$ structure. The following procedure was used. First systematic errors in d values were corrected by using the magnetite reflections as internal standards. Then values of a and c were derived for a hexagonal crystal, using the most accurately measured reflections. The five reflections used are marked in Table II; the best fit was achieved by using a least-squares program written here by Mrs. C. W. Pistorius for a Stantec Zebra electronic computer. Excellent agreement was obtained between the d values calculated on this basis and the measured d values of the reflections not considered in the derivation of a and c.

Calculation of Structure Factors.—The atomic parameters used in the calculation of structure factors were

6	Fe_{I}	in 6(c)	u_{I}	= 0.4563	w_{I}	= 0.318
6	Fe_{II}	in 6(c)	u_{II}	= 0.1219	w_{II}	= 0
6	Fe_{III}	in 2(b)	u_{III}	= 0.3333	w_{III}	= 0.818
6	C	in 6(c)	u_c	= 0.187	w_c	= 0.580

These are the coordinates of the Ru_7B_3 structure.[3] The atomic scattering factors were: Fe from Watson and Freeman.[16] Hönl correction $\Delta f' = -3.5$.[17] C from Berghuis, *et al.*[18] A single isotropic temperature factor $B = 3.0$ Å.^{2} was used.

The calculations were carried out on an IBM 704 computer, using Busing and Levy's program OR XLS.

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[17] M. J. Cooper, *ibid.*, **16**, 1067 (1963).

[18] J. Berghuis, IJ. M. Haanappel, M. Potters, B. O. Loopstra, C. H. MacGillavry, and A. L. Veenendaal, *ibid.*, **8**, 478 (1955).

Notes

CONTRIBUTION FROM NATIONAL ENGINEERING
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Fluoroalkyl Borate Esters[1,2]

BY H. LANDESMAN AND E. B. KLUSMANN

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There are two reports of fluoroalkyl borate esters in the literature. The first, tris(2,2,2-trifluoroethyl) borate, was prepared by Abel and co-workers[3] by the low temperature reaction of trifluoroethanol and boron trichloride in *n*-pentane. These workers reported a boiling point at reduced pressure for the compound and noted that it formed a coordination complex with pyridine. Schroeder[4] attempted the chlorination of several α,α-dihydrofluorinated borates, $(R_FCH_2O)_3B$, prepared in petroleum ether solution from boron trichloride and the alcohols.

Discussion

Fluoroalkyl Borates.—In the work reported here, a series of fluoroalkyl borates, $(H(CF_2CF_2)_xCH_2O)_3B$, where x = 1, 2, 3, and 4, has been prepared in yields up to 95% by direct reaction of the corresponding α,α,ω-trihydroperfluoroalkanols, $H(CF_2CF_2)_xCH_2OH$, and boron trichloride. Physical properties are listed in Table I.

The inductive effect of fluorine atoms on the alkyl groups of the borate ester should decrease interaction of unbonded oxygen electron pairs with the vacant p_z orbital of the boron atom in the esters. This decrease in "back bonding" should decrease boron shielding and the B^{11} n.m.r. chemical shift for the fluoroalkyl borate esters might be expected to be at lower fields than that for the alkyl borates. The B^{11} n.m.r. chemical shifts of alkyl borates and fluoroalkyl borates were found to be approximately equivalent ($\delta = -16.5$ to -18 p.p.m.)[5] so that if this effect prevails, it is not mirrored in the n.m.r. spectra.

Reaction of Fluoroalkyl Borates and Amines.—In work previously reported from this laboratory[6] the

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[1] This research was supported by Aeronautical Systems Division' Wright-Patterson Air Force Base, Dayton, Ohio, under Contract No. AF 33(657)-8015.

[2] This work was presented at the 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April, 1963.

[3] E. W. Abel, W. Gerrard, M. F. Lappert, and R. Shefferman, *J. Chem. Soc.*, 2895 (1958).

[4] H. Schroeder, *J. Org. Chem.*, **25**, 1682 (1960).

[5] T. P. Onak, H. Landesman, R. E. Williams, and I. Shapiro, *J. Phys. Chem.*, **63**, 1533 (1959).

[6] H. Landesman and R. E. Williams, *J. Am. Chem. Soc.*, **83**, 2663 (1961).

TABLE I

PHYSICAL PROPERTIES OF SOME FLUOROALKYL BORATES

	B.p., °C. (mm.)	Index of refraction	Density, g./cc.	Yield, %[a,b]
$[H(CF_2CF_2)CH_2O]_3B$	202–206 (748)	1.3294 (20°)	1.5717 (23°)	88.4
$[H(CF_2CF_2)_2CH_2O]_3B$	114 (1) 260–263 (745)	1.3210 (25°)	1.6964 (25°)	95.7
$[H(CF_2CF_2)_3CH_2O]_3B$	180–185 (3)	1.3210 (20°)	1.8156 (24°)	88.9
$[H(CF_2CF_2)_4CH_2O]_3B$	235–240 (2) M.p. 37–40°			

[a] Based on unrecovered alcohol. [b] The compound 2,2,3,3,4,4,5,5-octafluoroamyl borate was also prepared by transesterification of ethyl borate with 2,2,3,3,4,4,5,5-octafluoroamyl alcohol in the presence of titanium isopropoxide. The yield by this method was 45%, considerably lower than that from direct reaction of alcohol and boron trichloride.

formation of coordination compounds of alkyl borate esters with amines was investigated using B^{11} n.m.r. techniques for recognizing association of borate ester and amine. Though methyl borate reacted with hydrazine to form a coordination compound, the association of methyl borate with unsymmetrical dimethylhydrazine, a stronger base, was slight. Allyl borate, which also coordinated with hydrazine, showed no evidence of association with unsymmetrical dimethylhydrazine. Lack of reaction of the borates with unsymmetrical dimethylhydrazine was attributed to the steric effect of the alkoxy groups on boron.

With long chain fluoroalkyl borates available, it was of interest to determine whether the greater acidity of these borate esters, evidenced by Abel's report of reaction of trifluoroethyl borate with the weak base pyridine,[3] would outweigh the steric hindrance of the fluoroalkoxy groups to coordination compound formation.

By measuring B^{11} n.m.r. chemical shifts it was found that coordination occurred when 2,2,3,3-tetrafluoropropyl and 2,2,3,3,4,4,5,5-octafluoroamyl borates were allowed to react with hydrazine, unsymmetrical dimethylhydrazine, and even with pyridine. With 2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptyl borate reaction occurred with hydrazine and the stronger bases piperidine and pyrrollidine. The mixtures of the fluoroheptyl borate with unsymmetrical dimethylhydrazine and with pyridine were too viscous to give a signal and it was not possible to determine by n.m.r. whether reaction occurred.

Because the percentage of boron in 2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9-hexadecafluorononyl borate is so small and because viscous solutions were expected, the reactions of this borate with amines were not investigated using B^{11} n.m.r. It is to be noted that compound formation occurred where the boron was surrounded by three fluoroalkoxy chains each containing as many as seven carbon atoms. While unsymmetrical dimethylhydrazine will only associate slightly with methyl borate and not at all with allyl borate, it will form a coordination compound with 2,2,3,3,4,4,5,5-octafluoroamyl borate. Models indicate the steric strain should be large.

Reaction of Borate Esters with Boron Trifluoride and Boron Trichloride.—In other work on the use of B^{11} n.m.r. spectrometry to determine structures of boron compounds,[6] it was reported that the compounds formed from methyl, ethyl, propyl, or butyl borates with boron trifluoride at room temperature were alkoxydifluoroborane trimers rather than the previously reported coordination compounds of the borate with two molecules of boron trifluoride.

When attempts were made to prepare fluoroalkoxydifluoroborane trimers using fluoroalkyl borates and boron trifluoride, it was found that no reaction occurred at room temperature.

The reaction of boron trichloride with the alkyl borates yields either an alkoxydichloroborane monomer or a dialkoxychloroborane, dependent on reactant ratios. The alkoxydichloroborane exists as a monomer while the alkoxydifluoroborane trimerizes. The nonformation of a trimer in the alkoxydichloroborane is possibly due to steric crowding in the chloro compounds since the greater acid strength of boron–chlorine compounds should lead to stronger coordination than with the boron–fluorine compounds.

The fluoroalkyl borate esters react with boron trichloride to give the fluoroalkoxydichloroborane or bis(fluoroalkoxy)chloroborane. The materials were not isolated[7] but were identified by comparison of their B^{11} n.m.r. chemical shifts with those of authentic alkoxychloroboranes.[5] The chemical shift for the alkoxydichloroborane is at $\delta = -32.5$ p.p.m. and that for the dialkoxychloroborane is at $\delta = -23.3$ p.p.m. compared to the borate esters at $\delta = -16.5$ to -18 p.p.m.[5]

If the initial step in the mechanism of reaction of boron trichloride with the borate esters is the same as for boron trifluoride, that is, the coordination of the halide with the oxygen atoms in the borate, this work is additional evidence of the greater Lewis acidity of boron trichloride compared to boron trifluoride.[8] Boron trichloride will coordinate with weakly basic fluoroalkyl borate esters while boron trifluoride will not.

Experimental

(a) **Materials.**—The alcohols $H(CF_2CF_2)_nCH_2OH$, $n = 1, 2, 3$, or 4, were obtained from E. I. du Pont de Nemours and

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[7] Schroeder (ref. 3) prepared bis(1-chloro-2,2,3,3,4,4-heptafluorobutoxy)chloroborane from boron trichloride and tris(1-chloro-2,2,3,3,4,4,4-heptafluorobutyl) borate but was unable to obtain (1-chloro-2,2,3,3,4,4,4-heptafluorobutoxy)dichloroborane from the borate ester and excess boron trichloride.

[8] H. C. Brown and R. R. Holmes, *J. Am. Chem. Soc.*, **78**, 2173 (1956).

TABLE II

H^1 N.M.R. SPECTRA OF COMPOUNDS CONTAINING THE $\underset{\omega\ \ \omega-1}{HCF_2CF_2}(CF_2)_x\underset{\alpha+1\ \ \alpha}{CF_2CF_2}CH_2O$ GROUP

Compound		δ, p.p.m.	$J_{\omega F}$, c.p.s.	$J_{(\alpha+1)F}$, c.p.s. $J_{(\omega-1)F}$, c.p.s.	$J_{(\alpha+2)F}$, c.p.s.
$HCF_2CF_2CH_2OH$	αH	3.98		13.0 (α + 1)F	1.5 (ω) = (α + 2)
	ωH	5.94	54	4.5 (ω − 1)F	
	OH	4.46			
$H(CF_2)_4CH_2OH$	αH	4.12		15.5	...
	ωH	6.08	51.5	5.0	
	OH	4.72			
$H(CF_2)_6CH_2OH$	αH	4.12		15.0	...
	ωH	6.05	55.5	5.0	
	OH	4.65			
$[HCF_2CF_2CH_2O]_3B$	αH	4.25		13.0	...[a]
	ωH	5.87	54.0	4.0	
$[H(CF_2)_4CH_2O]_3B$	αH	4.39		13.0	...
	ωH	6.00	52.0	5.0	
$[H(CF_2)_6CH_2O]_3B$	αH	4.43		13.0	...
	ωH	5.98	51.5	5.0	

[a] The αH to (α + 2)F coupling is barely visible in this compound. Line broadening prevents its observation in the other compounds.

Company. Boron trichloride was obtained from the Matheson Company.

(b) **Typical Preparation: 2,2,3,3-Tetrafluoropropyl Borate.**—A Fisher and Porter Flowrator No. 08F-1/16-4/35 tube with glass ball float was calibrated by measuring the weight increase of pyridine used to absorb boron trichloride at various meter readings over timed intervals. In a 5-l. three-necked flask equipped with a stirrer, a reflux condenser protected with a Drierite drying tube, and a gas dispersion tube was put 3.71 kg. (28.1 moles) of 2,2,3,3-tetrafluoropropanol. The calculated amount of boron trichloride necessary to form the borate was metered into the alcohol over 9 hr. The flow rate varied during addition so that completeness of reaction was followed toward the end of the addition by infrared detection of the alcoholic OH band. The mixture was heated at approximately 60° for 2 hr. with a slow dry nitrogen sweep to remove dissolved hydrogen chloride and then distilled through a 65-cm. heated column packed with Raschig rings. Recovered was 814 g. of unreacted alcohol and 2.61 kg. (88.4%) of the borate ester, b.p. 202–206°.

Anal. Calcd. for $C_9H_9BF_{12}O_{13}$: B, 3.01. Found: B, 2.80. The analysis is obtained by titration of the boric acid from ester hydrolysis in the presence of mannitol. Other elemental analyses (C, H, F) were not satisfactory but structures are confirmed from the identity of the starting alcohols and the proton n.m.r. spectra of the products, *i.e.*, the OH peak due to alcohol disappears while the fluoroalkyl group spectrum remains. B^{11} n.m.r. chemical shifts are those expected for borate esters.[5,6,9] The proton spectra and coupling values are shown in Table II. No peaks due to species other than $H(CF_2CF_2)_xCH_2$ are seen.

(c) **Instrumentation.**—B^{11} n.m.r. spectra were obtained utilizing a Varian V-4300 high resolution n.m.r. spectrometer operating at 12.83 Mc. H^1 n.m.r. spectra were obtained utilizing a Varian A-60 high resolution n.m.r. spectrometer.

(d) **Reactions of Borates with Amines.**—Stoichiometric quantities of borate ester and amine were placed in n.m.r. sample tubes, and chemical shifts of the resultant solutions were measured utilizing boron trichloride and boron triethyl as standards.[5] Shifts, where reaction occurred, were at $\delta = -2$ to 0 p.p.m. compared to $\delta = -16$ to -18 p.p.m. for the borate.[6]

Acknowledgment.—The authors thank Professor Thomas P. Onak of the Los Angeles State College for stimulating discussions during this work.

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(9) W. D. Phillips, H. C. Miller, and E. L. Muetterties, *J. Am. Chem. Soc.*, **81**, 4496 (1959).

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Explosive Formation of Manganates under Very High Pressures

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In the course of a study of the behavior of solid oxidizing agents under very high pressures, the oxidation of MnO_2 by either $KClO_3$ or KNO_3 in the presence of alkali has been investigated. The oxidation of MnO_2 to K_2MnO_4 by $KClO_3$ or KNO_3 in the presence of KOH at atmospheric pressure is a well-known, solid-state method for preparation of the manganate. This study of the oxidation under very high pressures (10–50 kbars) has shown that the reaction becomes explosive at a comparatively low temperature (80–90°) above about 19 kbars.

Experimental

The high-pressure unit used in this work (Tem-Pres Research, Inc., Model SJ-100) was a uniaxial press with simple Bridgman anvils.[1] The reagents were thoroughly mixed in a mortar and the power was placed inside a nickel ring (0.75 in. o.d., 0.5 in. i.d., 0.018 in. thick) and sandwiched between two platinum covers 0.001 in. thick. Since the ratio between the internal diameter of the ring and its thickness was about 28, the pressure on the sample was essentially uniform along the ring diameter.[2] The sample and the anvils were heated by means of an external furnace. The temperature was measured by means of a chromel–alumel thermocouple placed in direct contact with the sample. The samples were brought to the desired pressure at room temperature and subsequently heated at constant pressure.

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(1) F. Dachille and R. Roy in "Modern Very High Pressure Techniques," R. H. Wentorf, Ed., Butterworths, London, 1962, p. 163.

(2) M. Myers, F. Dachille, and R. Roy, ASME Preprint No. 62-WA-255 (1962).