larly, for **1** ($R = C_2H_5$), $2\nu = 1340$ cm^{-1}. However, we are assuming that $^1A_1 \rightarrow {}^1A_2$ is not observed owing to small intensity. This is an unsafe assumption since a transition can gain considerable intensity by indirect means, *e.g.*, vibronic coupling. Thus the possibility that the higher energy band is $^1A_1 \rightarrow {}^1A_2$ ($\rightarrow {}^1B_1$ being masked by the ultraviolet tail) cannot be ruled out. With this assignment ν will have twice the previous value.

Comparison of the Nujol mull spectrum (bands at 14,930 and 17,540 cm^{-1}) of **1** ($R = CH_3$) with the solution spectrum shows a difference in splitting (Figure 1). For **1** ($R = C_2H_5$ and n-C_4H_9) mull and solution spectra are identical. We are unable to explain the anomaly of the methyl complex. The crystal structure is not known.

In conclusion, it may be mentioned that tris(benzoylacetonato)cobalt can be isolated[11] in *cis* and *trans* forms. They differ very little in absorption spectra and show an unsplit $^1A_1 \rightarrow {}^1T_1$ band in solution. This result is not surprising since the two types of oxygen atoms are expected to be very similar for crystal field purposes. However, the $^1A_1 \rightarrow {}^1T_1$ band of the very similar CoA_3 is known, from polarized spectral studies,[12] to be composite, the two components being separated by 800 cm^{-1}. The splitting is assigned to[12] the D_3 symmetry of the crystal field under which T_1 goes to $A_2 + E$. Particular mention of this observation is being made here because in the analysis of our results the chelate rings were completely neglected. Consideration of the chelate rings in **1** removes all symmetry; however, the number of bands predicted remains the same since all degeneracies are already lifted under C_{2v}. Interaction of metal d orbitals with the chelate rings, *e.g.*, *via* π bonding, can, of course, seriously affect the magnitude of splittings and intensities of the bands.

Complexes of Type 3.—In toluene **3** shows only one shoulder superimposed on an ultraviolet tail. Frequencies estimated visually are 20,000 cm^{-1} (ϵ 252) for $R = CH_3$ and 19,500 cm^{-1} (ϵ 257) for $R = CH(CH_3)_2$. No splittings were observed. Since all coordinating atoms are nitrogen, the rhombic component is probably small. A comparative study of the electronic spectra of pseudo-tetrahedral bis(salicylaldimine)cobalt(II) and bis(pyrrole-2-aldimine)cobalt(II) ($R = C(CH_3)_3$) has similarly shown a lower effective ligand field symmetry of the CoO_2N_2 *vs.* CoN_4 coordination sphere.[13] We assign the shoulder to the transition $^1A_1 \rightarrow {}^1T_1$. Setting the interelectronic parameter $C \approx 4000$ cm^{-1} (*i.e.*, same as for CoA_3), one obtains Dq (**3**) ≈ 2400 cm^{-1}. This may be compared with Dq of other CoN_6 complexes, *e.g.*, for $Co(NH_3)_6^{3+}$, $Dq = 2490$ cm^{-1}.[8] Assuming that C values for **1** and **3** are of similar magnitude and noting that the bands for **1** are all at lower energies than the single band of **3**, one concludes that pyrrole-2-aldimine creates a stronger effective ligand field than salicylaldimine.

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Vapor Phase Reaction between Anhydrous Aluminum Fluoride and Boron Oxide[1]

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Received May 2, 1966

The work of several authors[2-5] indicates that pure aluminum oxide, without contamination, can be obtained by vapor phase reactions. Most successful has been Schaffer,[5] who recently developed a chemical vapor-deposition technique for expitaxial growth of α-Al_2O_3 single crystals utilizing the reaction

$$2AlCl_3(g) + 3H_2(g) + 3CO_2(g) = Al_2O_3(s) + 3CO(g) + 6HCl(g) \qquad (1)$$

Oriented crystals weighing up to 5 g were grown by this method.

The purpose of this investigation was to carry out a simple reaction in the vapor phase in order to obtain aluminum oxide crystals, in such a way as to allow convenient doping of the crystals with various transition metal ions. It was suggested by the members of the solid-state research group at Du Pont[6] that the following reaction takes place in the vapor phase with the formation of aluminum oxide crystals

$$2AlF_3 + B_2O_3 = 2BF_3 + Al_2O_3 \qquad (2)$$

Since thermodynamic data are available for the compounds in the preceding equation, it is possible to calculate the standard free energy change ($\Delta G°$) and the equilibrium constant (K_p) for the reaction between 1000 and 2000°K and also to determine the optimum temperature for the formation of aluminum oxide.

It is well known that the aluminum oxide lattice is capable of accepting a variety of transition metal ions. The reaction between aluminum fluoride and boron oxide can be modified to produce doped crystals if a transition metal fluoride, for example, chromium(III) fluoride, is added to the aluminum fluoride. The thin platelets obtained by the vapor phase reaction are especially suitable for optical studies.

Experimental Section

Aluminum fluoride obtained commercially was not sufficiently pure to be used as a starting material. Aluminum fluoride can be purified by vacuum sublimation and such a procedure is described by Henry and Dreisbach.[7] Boron oxide is available as fused boric acid, but it must be fused again at 450° before it can be used.

The vapor phase reaction between aluminum fluoride and boron oxide was carried out as follows. Aluminum fluoride and boron oxide were contained in two separate crucibles, arranged

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[1] This work has been supported by the Air Force in Cambridge, Grant No. AF 19(628)-3837, and the National Science Foundation, Grant No. NSF GK-437.

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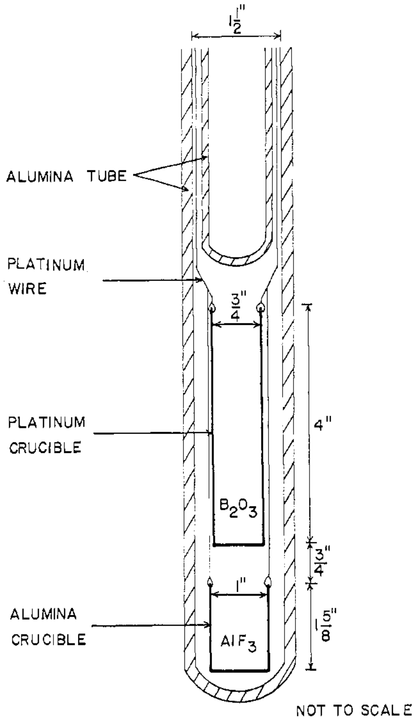

Figure 1.—Crystal growth apparatus.

vertically with boron oxide in the upper crucible (Figure 1). An alumina crucible of Type XN20 (Morganite) was used to hold the aluminum fluoride. The boron oxide was placed in a platinum crucible specially constructed for this experiment and measuring 0.75 in. in diameter and 4 in. in length. The reason for this exceptionally long crucible was to prevent boron oxide from boiling over and reacting with the aluminum fluoride in the solid (or liquid) state. The crucibles were suspended by platinum wires inside a long alumina tube with an inner diameter of about 1.5 in. A second alumina tube was fitted loosely inside the first one and acted as a stopper, but it was important that there was sufficient clearance between the two tubes for the boron fluoride formed in the reaction to escape.

The separation between the bottom of the upper crucible (holding boron oxide) and the lip of the lower crucible (holding aluminum fluoride) was set at 0.75 in. for most of the runs. The experiments were carried out with separations of 0.5 and 1 in., but no significant effect was observed in the crystal growth when the separation was so varied.

The reaction of aluminum fluoride and boron oxide was carried out at 1150° and allowed to proceed for approximately 20 hr. The time was not found to be critical.

Doping of the aluminum oxide crystals with different transition metal ions was possible by introducing the corresponding metal fluoride into the aluminum fluoride.

Results

When the reaction was carried out at 1150°, crystals in the form of thin platelets with a rhombohedral growth habit were found on the outer wall of the upper crucible and on the inner wall of the alumina tube containing the crucibles. At 1200° the crystals were located at a higher position along the crucible than at 1150°. It was found that below 1150° no crystals were formed, although a crust formed on the lip of the lower crucible. The crust was identified by X-ray diffraction to be aluminum borate ($9Al_2O_3 \cdot 2B_2O_3$).

The thin platelets of aluminum oxide measured up to 1 cm across. The form of the crystals was the same as those obtained by other authors,[2-4] but they were a number of times larger in size. Attempts were made to improve crystal growth by placing a seed crystal between the crucibles. It was found, however, that there was no apparent growth on the seed as reported by Shternberg and Kuznetsov.[4]

Both iron and chromium ions were successfully substituted into the aluminum oxide lattice when iron(III) fluoride or chromium(III) fluoride was mixed with aluminum fluoride. The resulting crystals of iron-doped crystals are green in color, while they are pink for chromium (ruby). From spectrographic analysis it was shown that approximately 2 wt % of iron is present in the iron-doped crystals and 0.3 wt % of chromium in chromium-doped crystals when 2 mole % of the corresponding metal fluoride is mixed with aluminum fluoride.

Discussion

The standard free energy change for the reaction

$$2AlF_3(g) + B_2O_3(g) = 2BF_3(g) + Al_2O_3(s) \qquad (3)$$

can be calculated since the standard free energy of formation for each constituent is known.[8, 9] Values of the equilibrium constant calculated from the standard free energy change are (T (°K), K_p): 1000, 2.32×10^{22}; 1100, 1.14×10^{19}; 1200, 2.03×10^{16}; 1500, 1.98×10^{10}; 2000, 2.39×10^{4}.

The reaction is exothermic, and the formation of aluminum oxide is favored at a lower temperature. However, the experiments showed that no crystals were formed below 1150°. This confirms the condition that the reaction has to be in the vapor phase. The rate at which aluminum fluoride sublimes below 1150° is not great enough to provide a significant vapor pressure for the vapor phase reaction (vapor pressure of aluminum fluoride at 1150° is 81 torr). Instead, the boron oxide vapor reacts with the solid aluminum fluoride forming a crust of aluminum borate on the lip of the crucible containing aluminum fluoride. A compromise is therefore necessary, and the most suitable temperature for the reaction appears to be 1150°.

There are no thermodynamic data available on chromium(III) fluoride within the temperature range of interest. Thus, it is not possible to calculate $\Delta G°$ and K_p for the formation of chromium(III) oxide, and the effect of temperature on chromium doping cannot be considered from a thermodynamic point of view.

The fact that the crystals obtained are a number of times larger than those obtained by other authors[2-4] suggests that it may be possible to grow even larger crystals by this method. This would require a larger reaction chamber and longer reaction times. In addition, better temperature control would undoubtedly reduce the number of nucleation centers, so that fewer but larger crystals would form.

It was demonstrated that it is possible to dope the

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(8) J. P. Coughlin, U. S. Bureau of Mines, Bulletin 542, U. S. Government Printing Office, Washington, D. C.

(9) "JANAF Thermochemical Tables," The Dow Chemical Co., Midland, Mich., PB-168370. The standard state chosen for gases is 298°K, 760 mm pressure.

aluminum oxide crystals with both iron and chromium ions, and it should be possible to extend the doping to all other transition metal ions, as long as the corresponding fluoride is available. Also, it is possible that this reaction may be modified by substituting aluminum fluoride with the various metal fluorides to give the corresponding metal oxides.

Acknowledgments.—The authors wish to thank A. L. Oppegard, W. C. Smith, and H. S. Young of E. I. du Pont de Nemours and Co. for suggesting the vapor phase reaction.

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Formation of Complex Fluoroborate Anions

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Received April 2, 1966

Complex fluorometallates or fluorometallate anions formed by sharing of fluorine atoms at a corner, edge, or face of a polyhedron containing the metal are well known. For example, AlF_4^- salts are formed by sharing of fluorine atoms at the edge of chains of the octahedra containing aluminum while AlF_5^- salts are formed by the sharing of a fluorine atom at the corners of long chains of the octahedra containing aluminum atoms.[1] Aluminum has been similarly reported to form anions of the type $Al_2Cl_7^-$ by sharing a chlorine atom.[2,3] Complex anions of similar types have not been reported involving boron trifluoride and the tetrafluoroborate anion,[3a] although complex borohydride anions including $B_2H_7^-$ are, of course, well-established.[4] Complex acids or salts of fluoroboric acid, *e.g.*, $K_4B_4F_{10}$, have been reported, but these salts are ill-defined and their existence is questionable.[5]

The boron trifluoride complexes of argon containing greater than 4 moles of boron trifluoride per mole of argon have been said to result from the addition of boron trifluoride molecules to fluorine atoms of the boron trifluoride molecules attached directly to the argon atom.[6] The strongly nucleophilic boron trifluoride molecule might also be expected to add to the negatively charged tetrafluoroborate anion giving a new species, $B_2F_7^-$. Further addition of boron trifluoride would give higher species such as $B_3F_{10}^-$ and $B_4F_{13}^-$. The absence of reports of adducts of this type indicates the tetrafluoroborate anion to be a very weak coordinating group, at least in its common environments.

We have found that certain amine tetrafluoroborate salts will absorb boron trifluoride to give the previously unreported $B_2F_7^-$ anion. The absorbed boron trifluoride can be removed quantitatively at reduced pressure with recovery of the original amine tetrafluoroborate salt. The amine salts investigated and the results at atmospheric pressure and 0° are shown in Table I.

TABLE I
ABSORPTION OF BORON TRIFLUORIDE BY AMINE TETRAFLUOROBORATE SALTS

Absorption	No absorption
$(C_2H_5)_3NH^+BF_4^-$	$C_2H_5NH_3^+BF_4^-$
$(i\text{-}C_3H_7)_2C_2H_5NH^+BF_4^-$	$sec\text{-}(C_4H_9)_2NH_2^+BF_4^-$
$(n\text{-}C_4H_9)_4N^+BF_4^-$	$(py)H^+BF_4^-$
	$(CH_3)_4N^+BF_4^-$

It is apparent from Table I that amine salts which will absorb boron trifluoride (at least at atmospheric pressure and 0°) contain relatively bulky cations. Thus the tetramethylammonium tetrafluoroborate salt gave no absorption of boron trifluoride while tetra-*n*-butylammonium tetrafluoroborate gave good boron trifluoride absorption. The tetrafluoroborate salts of bulky tertiary ammonium ions from triethylamine and diisopropylethylamine gave absorption of boron trifluoride, but the salt from the unhindered pyridinium cation gave no absorption of boron trifluoride. The critical factor is probably the distance between the tetrafluoroborate anion and the center of positive charge in the cation. When bulky cations are present the distance between the charged centers is increased to such an extent that the interaction of the cation and the tetrafluoroborate anion becomes relatively weak. The coordinating power of the tetrafluoroborate anion toward a nucleophile thus approaches its maximum potential value and it is able to coordinate with a free boron trifluoride molecule.

The mole ratio of absorbed boron trifluoride to salt is shown as a function of temperature in Table II.

TABLE II
MOLE RATIO OF ABSORBED BORON TRIFLUORIDE TO SALT

Salt	Temp, °C				
	0	25	50	75	100
$(i\text{-}C_3H_7)_2C_2H_5NH^+BF_4^-$	0.883	0.754	0.095	0.02	. . .
$(C_2H_5)_3NH^+BF_4^-$	0.891	0.712	0.542	0.369	0.236
$(n\text{-}C_4H_9)_4N^+BF_4^-$	1.01	1.00	1.00	0.772	0.699

In all instances the tetrafluoroborate salt was recovered quantitatively by placing the sample under reduced pressure at room temperature. It seems probable that at higher pressures and lower temperature further addition of boron trifluoride to the $B_2F_7^-$ anion to form species such as $B_3F_{10}^-$, etc., might occur.

The absorption of boron trifluoride causes several changes in the physical properties of the salt. These are as follows.

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