divalent metal chlorides all had a single crystal form with the exception of $ZnCl_2$.[9] These facts simplified the interpretation of the X-ray powder data. In the absence of polymorphic forms of the pure components, the appearance of new lines must be attributed to compound formation between divalent metal chloride and $AlCl_3$. Table I is a list of the systems studied and the general results as determined by X-ray examination of the fused product. The color of the fused system was characteristic of the initial divalent chloride although much deeper. The X-ray powder patterns definitely showed compounds formed only after the fusion process. For Mg and Co, the pure products were able to be isolated. In these materials the compound formation and type were verified by chemical analyses. It is interesting that not all systems formed compounds in the fused state. Repeated trials over wide composition ranges were performed for Be, Zn, Ti, Hg, and Pt. In the first two cases glass formation was encountered and special recrystallization techniques may be necessary to obtain compounds. The last three cases always ended with slurries of the metal chloride in $AlCl_3$ at elevated temperatures. The systems which formed compounds gave uniform solutions at elevated temperatures.

Table II is a list of the powder patterns derived from the fifteen systems which formed compounds. The data for the Co, Mg, V, Cr, Mn, and Fe systems revealed that these formed closely related structures or possibly an isomorphous series. The strongest line consistently appears at a spacing of 2.83–2.89 Å. The initial pairs of lines are likewise similar in their intensities and spacings. Other recurrent spacings are found near 3.26, 2.21, 1.87, and 1.69 Å. In addition, the ionic radii[10] of these six divalent metals are all 0.77 ± 0.12 Å. so that spatial requirements can be readily fulfilled. The cobalt structure has already been determined[5] to be of the 1:2 type. Therefore, it is suggested that the other five systems have a similar composition, $M(AlCl_4)_2$, where M is the divalent metal. The powder pattern of $Co(AlCl_4)_2$ can be readily indexed from the unit cell dimensions and intensities reported by Ibers.[5] The first entry of Table II gives these results.

Little is known about the composition or structures of the remaining nine systems of Table II. For $CdCl_2$–$AlCl_3$ the compound is of the 1:2 type[4] but not isostructural with $Co(AlCl_4)_2$. Considerable changes of spacings and intensities are noted in the respective powder patterns. These changes argue against the indexing of the $Cd(AlCl_4)_2$ compound from the unit cell dimensions of the $Co(AlCl_4)_2$. The larger ionic radius of Cd^{2+} (0.97 Å.) must also influence the structural packing. The powder pattern for the Cd system is the same as that previously listed.[4] All other systems in Table II must possess a variety of compositions and structures when judged from the powder data. Individual phase diagrams and single crystal data are both needed to

complete the study. Meaningful conclusions could then be drawn.

The Preparation of Some Alkali Hexabromotitanates(IV)

By Klaus F. Guenther

Previous investigations have shown that some monovalent metal chlorides react with titanium tetrachloride in fused antimony trichloride to give the corresponding metal hexachlorotitanates(IV).[1] Now we have found that alkali metal bromides react in a similar manner with titanium tetrabromide in fused antimony tribromide to form alkali hexabromotitanates(IV). Only compounds of the type $(AH)_2TiBr_6$ (where $A = NH_3$, C_5H_5N, C_9H_7N) have been described in the literature.[2,3]

Alkali metal bromides (except lithium bromide and sodium bromide) and titanium tetrabromide are readily soluble in fused antimony tribromide,[4] and the alkali hexabromotitanates formed are only slightly soluble in the melt. After solidification of the antimony tribromide melt, the excess titanium tetrabromide and the antimony tribromide can be easily removed with an organic solvent, which does not dissolve the alkali hexabromotitanates. Potassium hexabromotitanate-(IV), rubidium hexabromotitanate(IV), and cesium hexabromotitanate(IV) were prepared by this technique.

Experimental

The experimental procedure was the same as described earlier[1] with the following exceptions. Approximately 0.4 g. of alkali metal bromide was dissolved in about 50 g. of double-distilled $SbBr_3$, and the reactions were performed at approximately 110° for periods up to 48 hr. The product salts sometimes contained small amounts of unreacted alkali metal bromide when shorter heating periods were used. The reaction products were extracted in an erlenmeyer flask with distilled, dry CS_2 by repeated decanting of the organic solvent from the insoluble phase, which settled at the bottom of the flask.

Results and Discussion

The salts K_2TiBr_6, Rb_2TiBr_6, and Cs_2TiBr_6 were prepared by using fused $SbBr_3$ as the solvent. *Anal.* Calcd. for K_2TiBr_6: K, 12.91; Ti, 7.92; Br, 79.17.

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Found: K, 12.6; Ti, 7.8; Br, 78.9. Calcd. for Rb_2-$TiBr_6$: Rb, 24.48; Ti, 6.86; Br, 68.66. Found: Rb, 24.2; Ti, 6.8; Br, 68.3. Calcd. for Cs_2TiBr_6: Cs, 33.51; Ti, 6.04; Br, 60.45. Found: Cs, 33.1; Ti, 5.9; Br, 60.2. All compounds obtained were dark wine-red. The rubidium salt was darker than the potassium and cesium salts.

The alkali hexabromotitanates appear to be stable in dry air. However, they are rapidly decomposed when exposed to the atmosphere in the laboratory ($\sim$60% relative humidity). The alkali hexabromotitanates are considerably more hygroscopic than the corresponding hexachlorotitanates. The hygroscopicity decreases from the potassium to the cesium salt.

In preliminary X-ray studies it was found that the potassium, rubidium, and cesium hexabromotitanates are isomorphous with potassium hexachloroplatinate. The lattice constants of the potassium, rubidium, and cesium hexabromotitanates were found to be a_0 = 10.35, 10.46, and 10.66 Å., respectively.

The formation of the alkali hexabromotitanates in fused antimony tribromide and the formation of the monovalent metal hexachlorotitanates in fused antimony trichloride[1] are based on a similar acid–base reaction. Another type of acid–base reduction in fused antimony tribromide was described by Jander and Weis.[5]

Acknowledgment.—Miss Irene Corvin performed the X-ray analyses.

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Infrared Spectra of Vanadium Fluorides

BY R. G. CAVELL AND H. C. CLARK

Although the chemistry of the higher fluorides of vanadium has been extensively investigated[1,2] and certain physical properties have been determined,[3,4] little structural information has yet been obtained. The structure of vanadium pentafluoride is of some considerable interest since the liquid is thought to be associated[1,5] by fluorine bridge bonds, while the normal vapor density[1,6] suggests that the pentacoordinate monomer is present in the gas phase. Moreover, the geometry of this monomer, either trigonal bipyramidal or perhaps square pyramidal, is itself of great interest.

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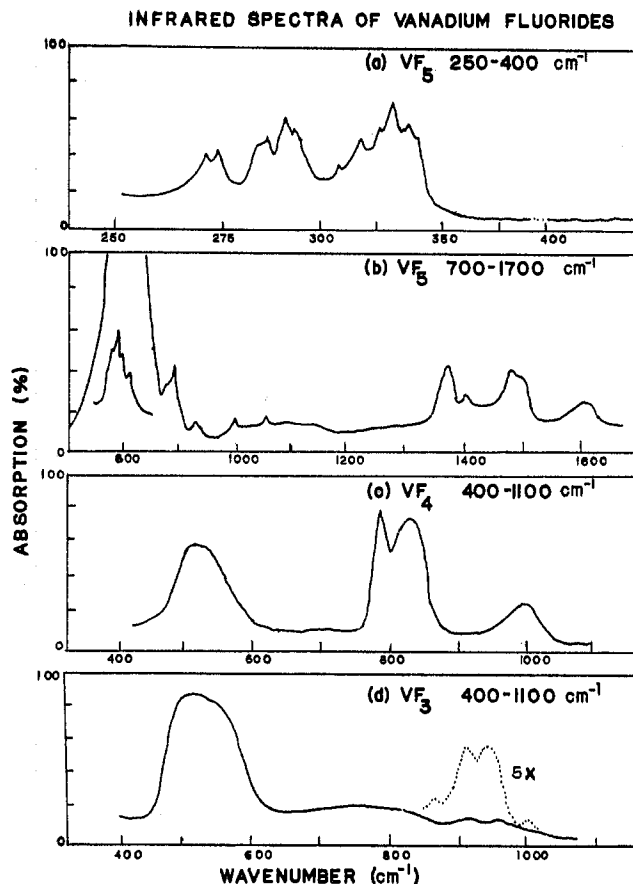

Figure 1.

Since there are no nonbonding, valence-shell electron pairs in vanadium pentafluoride, the trigonal bipyramidal structure is reasonably expected, but this has not yet been established for this or any other transition metal fluoride. As one approach, we have now investigated the infrared spectrum of vanadium pentafluoride, and also of the tetra- and trifluorides.

Experimental

The preparations of vanadium pentafluoride and tetrafluoride have been described previously,[1,2] as well as the techniques involved in their manipulation. Vanadium trifluoride was obtained by the thermal decomposition of the tetrafluoride.[2] The infrared spectra were measured on Perkin-Elmer Model 21 infrared recording spectrometers, fitted with NaCl optics for the 650–4000 cm.$^{-1}$ region and cesium bromide optics for 200–650 cm.$^{-1}$. Spectra of the pentafluoride were taken using two different gas cells. The first was a 9-cm. long stainless steel cell fitted with polyethylene windows 0.5-mm. thick and held in place by stainless steel compression rings. With this cell, the 200–1000 cm.$^{-1}$ region could be observed, since polyethylene has only two weak absorption bands at 720 and 730 cm.$^{-1}$. The other was a 10-cm. glass cell fitted with potassium bromide plates which previously had been coated with a thin film of paraffin wax to prevent attack by the pentafluoride. These windows were transparent from 350 to 4000 cm.$^{-1}$, except for the sharp paraffin absorption bands at approximately 2900, 1400, 730, and 720 cm.$^{-1}$ which were weak because of the thinness of the wax film and hence did not obscure a large region of the spectrum.

Both cells were attached to glass fingers into which the pentafluoride was distilled. The pressure of pentafluoride vapor within the cell could be controlled by cooling the finger to various temperatures. Spectra were measured on two different samples in each cell over the entire accessible range for each cell, with no appreciable differences being observed.