identified by X-ray powder diffraction analysis. Less extensive washing leaves the precipitate associated with sodium carbonate or sodium hydroxide. This dilemma prevents the establishment of the composition of the boride by direct chemical means either at the stage of metal precipitation or at any successive stage.

X-Ray powder diffraction analyses proved that the initial precipitate as washed in cold water is amorphous. The diffraction pattern showed only a broad halo with a maximum corresponding to an interplanar spacing of $\sim$2.03 Å. (see Table I). The breadth of the halo indicates a crystallite size of about 15 Å. diameter, a value which corresponds to a surface area of about 1200 m.^{2}/g.

Thermal treatment of the precipitate at 250° causes recrystallization to the Rundquist[6] and Fruchart[7] structure and metallic nickel (Table I).

X-Ray powder diffraction analysis gave the pattern reported in Table II, where it is compared with that of the Ni_3B of Fruchart.[7] The correspondence is so close even in the back reflection region that not only must the structures be the same but also the lattice parameters must correspond to within ± 0.002 Å.

The recrystallization to the Rundquist[6] Ni_3B and metallic nickel also occurred at temperatures as high as 750°, and this confirms both Anderson and Kiessling's[8] and Rundquist's[6] observations that Ni_3B is stable at this temperature.

Diffraction analysis of the precipitate after washing at 80° shows the presence of metallic nickel in the face-centered cubic form as indicated by 111, 200, 220, 311, and 222 reflections. The broad halo at 203 Å. was still present. The precipitate at this stage must be regarded as metallic nickel accompanied by amorphous material.

Attempts to recrystallize the precipitate as prepared from the acetate at 200° and below failed.

Although the diffraction pattern of Bjurstrom's[9] Ni_2B with lattice parameters $a_0 = 4.980$ and $c_0 = 4.236$ Å. and space group $D_{4h}{}^{18}$ was sought, no trace was found in any of the present preparations.

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[7] R. Fruchart, *Ann. Chim.*, **4**, 1247 (1959).
[8] L. H. Anderson and R. Kiessling, *Acta Chem. Scand.*, **4**, 160 (1950).
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CONTRIBUTION FROM GOODRICH–GULF CHEMICALS, INC.,
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BRECKSVILLE, OHIO

Preparation and X-Ray Data of Compounds Formed in Divalent Metal Chloride–Aluminum Chloride Fused Salt Systems

BY ROGER F. BELT[1] AND HARVEY SCOTT

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The first compounds of $AlCl_3$ combined with divalent metallic chlorides (MCl_2) were apparently prepared by Baud[2] and characterized by thermal data. A more thorough study of fused salt systems of $AlCl_3$ with metallic chlorides was made by Kendall, Crittenden, and Miller,[3] who attempted to enumerate the main factors which governed compound formation and solubility behavior. Further general work seems to have been abandoned except for single systems. The $CdCl_2$–$AlCl_3$ system has been examined with X-ray techniques and a powder pattern listed.[4] Recently a complete structure determination of the compound $Co(AlCl_4)_2$ was reported.[5] The present work covers in detail the preparation, X-ray powder data, and a discussion of compounds in many additional systems.

TABLE I

FUSION RESULTS OF MIXED SYSTEMS

Divalent chloride fused with $AlCl_3$	Color of product	Type of compd.[c]
$MgCl_2$	White	1–2[a]
$CaCl_2$	White	Unknown
VCl_2	Violet	1–2[b]
$CrCl_2$	Violet	1–2[b]
$MnCl_2$	Pink	1–2[b]
$FeCl_2$	Yellow-green	1–2[b]
$CoCl_2$	Blue	1–2[a]
$NiCl_2$	Green	Unknown
$CuCl_2$	Yellow-brown	Unknown
$SrCl_2$	White	Unknown
$CdCl_2$	White	Probably 1–2
$BaCl_2$	White	Unknown
$SnCl_2$	White	Unknown
$PbCl_2$	White	Unknown
$PdCl_2$	Red	Unknown

[a] By chemical analysis. [b] From similarity of powder patterns. [c] Experiments with the chlorides of Be, Zn, Ti, Hg, and Pt showed no compound formation.

Experimental

Anhydrous salts were used for all preparations and commercial reagent grades were utilized when available Several compounds were prepared by thermal decomposition of hydrates. The X-ray powder diffraction pattern of each substance was taken, and the lines were compared with standard patterns. If any unexplained lines were present, the material was rejected or purified further. The aluminum chloride was not purified even though it was evident from thermal discoloration that small amounts of $FeCl_3$ (*ca.* 0.01%) or other decomposable salts were present. These slight impurities could in no manner affect the reported results.

Compounds were prepared by weighing out the initial reactants and inserting them in heavy-walled Pyrex glass tubes. All operations were performed in a glove box purged with dry nitrogen and dried with P_2O_5. The tubes were sealed and reaction was effected by heating over a flame or in a capped metal tube. Temperatures were always above the melting point of $AlCl_3$. In cases where compounds were formed, a clear solution was usually obtained but not always. Initial experiments were confined to compositions involving molar ratios of 1:2 for MCl_2:$AlCl_3$. Additional samples over the composition range of 1:3 to 3:1 were then chosen for each system. The X-ray results showed the same *d* spacings independent of the charged composition. However, they do not preclude other compounds in narrow composition ranges bordering the pure components.

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[1] The Harshaw Chemical Company, Cleveland, Ohio.

[2] E. Baud, *Compt. rend.*, **133**, 869 (1901); *Ann. Chem.*, [8] **1**, 8 (1904).

[3] J. Kendall, E. D. Crittenden, and H. K. Miller, *J. Am. Chem. Soc.*, **45**, 963 (1923).

[4] J. D. Corbett, W. J. Burkhard, and L. F. Druding, *ibid.*, **83**, 76 (1961).

[5] J. A. Ibers, *Acta Cryst.*, **15**, 967 (1962).

TABLE II

X-RAY POWDER DATA OF FUSED SYSTEMS

Fused $CoCl_2 + AlCl_3$					Fused $MgCl_2 + AlCl_3$		Fused $VCl_2 + AlCl_3$	
d, Å. obsd.[a]	*d*, Å. calcd.[b]	*hkl*	I/I_0 obsd.[a]	I/I_0 calcd.[c]	*d*, Å.	I/I_0	*d*, Å.	I/I_0
6.56	6.63	110	0.7	0.4	6.75	0.3	6.55	0.8
6.33	6.40 + 6.39	200 + 011	0.9	0.7	6.41	0.3	6.35	0.8
4.45	4.36	202	0.2	0.2	5.86	0.6	5.82	0.6
4.17	4.19	$20\bar{2}$	0.1	0.1	5.03	0.2	4.48	0.2
3.71	3.74	310	0.3	0.1	4.55	0.2	4.15	0.1
3.57	3.58	311	0.1	0.1	3.45	0.2	3.70	0.2
3.43	3.43	013	0.1	0.1	3.36	0.3	3.45	0.2
3.29	3.31	220	0.4	0.1	3.21	0.3	3.30	0.4
3.18	3.20 + 3.21	400 + 022	0.6	0.3	2.89	1.0	3.18	0.6
2.87	2.89 + 2.87	222 + 004	1.0	1.0	2.79	0.2	2.90	0.6
2.83	2.84	$22\bar{2} + 402$	0.1	0.2	2.45	0.8	2.83	1.0
2.74	2.75	$40\bar{2}$	0.1	0.3	2.21	0.2	2.78	0.1
2.38	2.39	230	0.1	0.1	2.16	0.2	2.44	0.6
2.27	2.29	024	0.1	0.1	2.02	0.1	2.19	0.4
2.19	2.21 + 2.18 + 2.19	$51\bar{2} + 404 + 224$	0.1	0.4	1.96	0.2	2.15	0.4
2.14	2.15	$22\bar{4}$	0.2	0.1	1.88	0.3	2.02	0.1
2.02	2.02	611	0.2	0.1	1.76	0.2	1.93	0.4
1.93	1.94 + 1.92	040 + 006	0.4	0.1	1.71	0.3	1.86	0.6
1.86	1.87 + 1.85	620 + 240	0.8	0.2	1.69	0.3	1.73	0.1
1.81	1.82	530	0.1	0.1	1.65	0.2	1.71	0.2
1.77	1.77	710	0.1	0.1	1.62	0.1	1.68	0.2
1.71	1.72	316	0.2	0.1	1.55	0.1	1.65	0.1
1.67	1.67	406 + 226	0.3	0.2	1.52	0.1	1.59	0.1
1.64	1.64	$22\bar{6}$	0.1	0.1	1.47	0.1	1.45	0.1
1.59	1.59	624	0.1	0.1	1.40	0.1	1.39	0.1
1.53	1.54	150	0.1	0.1	1.28	0.1		
1.48	1.48	820	0.1	0.1				
1.18	1.18	$102\bar{2}$	0.2	0.1				
1.15	1.15 + 1.16	048 + 628	0.2	0.1				

Fused $CrCl_2 + AlCl_3$		Fused $MnCl_2 + AlCl_3$		Fused $FeCl_2 + AlCl_3$		Fused $CdCl_2 + AlCl_3$	
d, Å.	I/I_0	*d*, Å.	I/I_0	*d*, Å.	I/I_0	*d*, Å.	I/I_0
6.60	0.8	6.70	0.6	6.73	0.4	6.97	0.8
6.32	0.8	6.37	0.6	6.42	0.4	6.44	0.8
4.92	0.2	4.55	0.2	4.46	0.1	5.87	1.0
3.26	0.2	3.75	0.2	4.11	0.4	4.57	0.8
3.01	0.2	3.48	0.1	3.72	0.2	3.59	0.6
2.86	1.0	3.36	0.4	3.46	0.2	3.18	0.4
2.47	0.1	3.21	0.4	3.34	0.2	3.01	0.4
2.23	0.3	2.89	1.0	3.21	0.2	2.88	0.8
1.87	0.3	2.85	0.6	2.85	1.0	2.70	0.2
1.70	0.3	2.74	0.1	1.87	0.2	2.57	0.2
1.37	0.2	2.17	0.2	1.69	0.2	2.46	0.2
		2.03	0.1			2.39	0.4
		1.97	0.4			2.30	0.2
		1.88	0.9			2.23	0.6
		1.73	0.1			2.07	0.2
		1.69	0.1			2.02	0.2
		1.66	0.1			1.90	0.6
		1.62	0.2			1.76	0.1
		1.43	0.1			1.72	0.4
						1.69	0.1
						1.67	0.1
						1.55	0.1
						1.51	0.1
						1.49	0.1
						1.43	0.2
						1.29	0.1
						1.27	0.1
						1.25	0.1

X-Ray powder photographs were obtained with a General Electric 14-cm. diameter camera. The effective diameter was determined with a NaCl standard. Film shrinkage was also estimated by use of $AlCl_3$ mixed with the specimens. Samples were powdered, loaded into 0.2-mm. diameter glass capillaries, and then sealed. Operations were performed in a drybox. Nickel-filtered copper radiation (λ 1.5418 Å.) was used for all samples except Co- or Fe-containing samples. For these systems iron-filtered cobalt radiation (λ 1.7902 Å.) was chosen. Intensities were visually estimated and uncorrected for specimen absorption.

TABLE II (*Continued*)

Fused $CaCl_2 + AlCl_3$		Fused $NiCl_2 + AlCl_3$		Fused $CuCl_2 + AlCl_3$		Fused $SrCl_2 + AlCl_3$	
d, Å.	I/I_0	*d*, Å.	I/I_0	*d*, Å.	I/I_0	*d*, Å.	I/I_0
9.29	1.0	6.35	0.4	6.53	0.4	6.30	0.9
6.85	0.4	5.81	1.0	5.87	1.0	5.83	0.6
6.24	0.6	5.07	0.4	5.13	0.2	4.97	0.8
5.83	0.6	4.80	0.2	4.90	0.2	4.04	0.4
4.86	0.2	3.24	0.2	4.65	0.4	3.79	0.4
4.57	0.1	3.10	0.2	3.92	0.2	3.60	0.4
3.65	0.1	2.95	0.4	3.56	0.2	3.39	0.4
3.41	0.1	2.91	0.6	3.20	0.1	3.15	1.0
3.28	0.1	2.80	0.6	3.05	0.1	2.92	0.6
3.11	0.6	2.73	0.4	2.91	0.6	2.79	0.6
2.92	0.6	2.46	0.9	2.81	0.8	2.60	0.2
2.79	0.6	2.27	0.1	2.45	0.8	2.54	0.2
2.48	0.8	2.12	0.1	2.25	0.4	2.46	0.9
2.32	0.1	1.94	0.2	2.16	0.4	2.31	0.4
2.25	0.1	1.91	0.4	1.91	0.2	2.27	0.4
1.76	0.1	1.76	0.6	1.88	0.2	1.91	0.1
1.70	0.2	1.73	0.6	1.84	0.4	1.79	0.1
1.64	0.1	1.70	0.6	1.76	0.6	1.76	0.1
1.47	0.1	1.66	0.4	1.71	0.8	1.71	0.4
1.40	0.1	1.63	0.1	1.64	0.2	1.56	0.1
1.11	0.1	1.47	0.2	1.61	0.2	1.51	0.1
1.08	0.1	1.46	0.4	1.48	0.4	1.45	0.1
		1.44	0.4	1.46	0.4	1.40	0.2
		1.42	0.4	1.40	0.6	1.26	0.1
		1.40	0.4	1.28	0.1	1.20	0.1
		1.28	0.1	1.22	0.2	1.11	0.1
		1.23	0.2	1.17	0.1	1.08	0.1
		1.11	0.4	1.11	0.2		
		1.10	0.2	1.08	0.2		
		1.08	0.2				

Fused $BaCl_2 + AlCl_3$		Fused $SnCl_2 + AlCl_3$		Fused $PbCl_2 + AlCl_3$		Fused $PdCl_2 + AlCl_3$	
d, Å.	I/I_0	*d*, Å.	I/I_0	*d*, Å.	I/I_0	*d*, Å.	I/I_0
7.56	1.0	6.17	1.0	7.25	0.6	6.47	1.0
5.83	0.6	5.85	0.8	6.10	1.0	5.84	0.8
5.28	0.6	5.19	0.6	5.21	0.6	4.89	0.8
4.60	0.8	4.59	0.1	4.57	0.2	4.68	0.2
3.54	0.1	3.87	0.4	4.04	0.2	4.47	0.4
3.23	0.1	3.53	0.1	3.83	0.6	4.06	0.2
2.92	0.4	3.40	0.1	3.48	0.4	3.77	0.4
2.82	0.4	3.18	0.2	3.34	0.4	3.37	0.1
2.61	0.2	3.07	0.2	3.04	0.4	3.18	0.4
2.51	0.2	2.97	0.1	2.92	0.2	2.92	0.8
2.45	0.2	2.92	0.4	2.69	0.4	2.81	0.6
2.17	0.4	2.86	0.1	2.55	0.6	2.45	0.1
2.01	0.1	2.80	0.4	2.47	0.6	2.35	0.1
1.85	0.1	2.74	0.2	2.39	0.2	2.02	0.1
1.74	0.1	2.60	0.4	2.30	0.2	1.86	0.1
1.71	0.2	2.56	0.1	2.27	0.2	1.82	0.1
1.55	0.1	2.51	0.4	2.15	0.4	1.71	0.6
1.51	0.1	2.45	0.4	2.11	0.4	1.64	0.1
1.40	0.1	2.36	0.1	1.90	0.1	1.47	0.1
		2.31	0.1	1.71	0.1	1.40	0.1
		2.19	0.1	1.68	0.1	1.11	0.1
		2.14	0.1	1.60	0.2	1.08	0.1
		1.76	0.2	1.49	0.1		
		1.70	0.4	1.42	0.1		
		1.40	0.2	1.37	0.1		
		1.11	0.2				
		1.09	0.2				

[a] Powder data of authors. [b] From unit cell data and indices in ref. 5. [c] From F_0^2 values reported in ref. 5 corrected using Lorentz-polarization and multiplicity factors. About 100 of the strongest reflections were computed.

Results and Discussion

Several investigations[6,7] have shown that $AlCl_3$ consists of only one phase in the solid. No other crystal forms have been reported and the structure described by Ketelaar and co-workers[8] has been the best obtained to date. A survey of the literature showed that the simple

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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.

Acknowledgment.—The authors are grateful to the B. F. Goodrich Co. and Goodrich–Gulf Chemicals, Inc., for permission to publish this note.

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CONTRIBUTION FROM THE IIT RESEARCH INSTITUTE,
CHICAGO, ILLINOIS

The Preparation of Some Alkali Hexabromotitanates(IV)

BY KLAUS F. GUENTHER

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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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