[CONTRIBUTION FROM THE BELL TELEPHONE LABORATORIES, INC.]

Growth of Single Crystal Rare Earth Orthoferrites and Related Compounds

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A method for the synthesis and growth of single crystals of rare earth orthoferrites and related compounds having the general formula $A^{+3}B^{+3}O_3^{-2}$ is presented. Forty-two compounds have been prepared as small single crystals. Chemical analysis of the rare earth orthoferrite crystals is given.

Introduction

A considerable amount of work has been done by L. Néel[1] and Paúthenet and Blum,[2] among others, on the magnetic properties of $GdFeO_3$, one of the rare earth orthoferrites. X-Ray examinations of many of these perovskite-like compounds by Naray-Szabō,[3,4] Megaw,[5] Ruggiero and Ferro,[6] and by Yakel,[7] have almost all been carried out on reacted powders, with the usually attendant difficulties. An attempt was made here to produce single crystals of these compounds because of an increased interest in their properties.

Some success has been attained by the author in growing single crystals of some of the spinel ferrites of the type AFe_2O_4 using lead monoxide as a solvent at high temperatures.[8] It was thought then that this solvent might be suitable for the solution and crystallization of the rare earth orthoferrites and related compounds. This proved to be the case and small single crystals of the type A^{+3}-$B^{+3}O_3^{-2}$ were obtained, with Y, La, Pr, Nd, Eu, Sm and Gd in the A position and Al, Sc, Cr, Fe, Co and Ga in the B position.

The crystal structure of $GdFeO_3$ has been reported by Geller[9] and extensive crystallographic data on several orthoferrites, orthochromites and other compounds are reported in a paper soon to be published by Geller and Wood.[10] Magnetic properties of a $GdFeO_3$ crystal have been investigated by Gilleo.[11] These investigations have been made at these laboratories as part of our interest in perovskite-like structures.

Method.—The rare earth oxides used were the 99% pure variety and all other chemicals were reagent grade. Equimolar proportions of the constituent oxides were weighed into a pure platinum crucible. Lead monoxide was added in the ratio of constituent oxides to lead monoxide at 1:6 by weight. Anticipated experiments did not require large crystals so a dilute melt was made to ensure complete solution. No attempt was made to determine the degree of saturation at any given temperature. The crucibles were covered and placed in a horizontal glo-bar type furnace equipped with a silicon carbide muffle with a mullite floor plate. Furnace temperature at the time of loading was 1300°. The atmosphere was not controlled. Holding time at solution temperature was held to a minimum to prevent excessive loss of the PbO by volatilization. Solution for the concentration ratio 1:6 for a charge mass of 90 g. was found to be complete at 1300° in about one hour. The temperature was reduced in a uniform manner at about 30°/hour to below the solidification temperature, which is about 850°. The crucibles were then removed and allowed to cool quickly to room temperature. The mass thus obtained, consisting of solidified PbO and crystals of the sought compound, was leached out with a hot dilute solution of nitric acid. The crystals, which are not attacked by nitric acid, were thoroughly washed in distilled water and dried.

Chemical Analysis.—Qualitative spectrochemical analysis revealed the presence of Pb and Pt as impurities. The amount of Pt found was in the order of 0.05% for all the orthoferrites. Some platinum impurity may be expected when the crystallization has been carried out in a platinum crucible at high temperatures. Lead analysis varied considerably from sample to sample. Some samples analyzed as high as 1.5% Pb. This apparently was caused by the trapping of PbO within the crystals as a result of the rapid rate of crystallization. When the crystals were crushed and treated with HNO_3 to remove the included PbO, the concentration of Pb was found to be about 0.5%. It is speculative at this point as to whether some lead is entering the structures in place of the rare earth. The weight percentages of rare earth and iron found by quantitative chemical analysis are given in Table I. The results are compared with the calculated values. The rare earth analysis is reported as total rare earth found and has been calculated as the designated rare earth. Qualitative spectrochemical analysis showed that indeed the principal rare earth present was that which was designated.

TABLE I

QUANTITATIVE CHEMICAL ANALYSIS OF THE ORTHOFERRITES

	Analyzed		Calcd.	
	Rare earth (±0.1)	Iron (±0.05)	Rare earth	Iron
Y	47.54	25.75	46.13	28.97
La	56.54	21.90	57.23	23.00
Pr	59.34	21.40	57.58	22.81
Nd	55.75	21.21	58.15	22.51
Sm	56.56	22.28	59.16	21.96
Eu	54.80	20.14	59.41	21.82
Gd	58.52	21.88	60.18	21.42

Related Compounds.—The closely related compounds, where Fe^{+3} is replaced by either Al^{+3}, Sc^{+3}, Ga^{+3} or Co^{+3}, were crystallized in much the same manner as the orthoferrites. One notable difference was that in the case of the Al^{+3} and Sc^{+3} substitutions, the holding time at the solution temperature had to be increased to about 4 hours due to the slow rate of solution of these highly refractory oxides.

When the rare earth orthochromites, where Fe^{+3} is replaced by Cr^{+3}, were attempted, it was found that the reaction of PbO with Cr_2O_3 produced stable lead chromates, preventing formation of the desired compounds. These compounds were crystallized using bismuth trioxide instead of lead monoxide as the solvent, with all other conditions such as concentration, temperature, etc., remaining the same. The resulting crystals of ortho-

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[1] L. Néel, *Compt. rend.*, **239**, 8 (1954).

[2] P. Paúthenet and P. Blum, *ibid.*, **239**, 33 (1954).

[3] St. V. Naray-Szabō, *Naturwiss.*, **31**, 202, 466 (1943).

[4] St. V. Naray-Szabō, *Publ. Univ. Tech. Sci., Budapest*, **1**, 30 (1947).

[5] H. D. Megaw, *Proc. Phys. Soc.*, **58**, 133 (1946).

[6] A. Ruggiero and R. Ferro, *Atti della Accad. Nazionale di Lincei*, **XVII**, 254 (1954).

[7] H. L. Yakel, Jr., *Acta Cryst.*, **8**, 394 (1955).

[8] To be published.

[9] S. Geller, *J. Chem. Phys.*, **24**, 1236 (1956).

[10] S. Geller and E. A. Wood, *Acta Cryst.*, in press.

[11] M. A. Gilleo, *J. Chem. Phys.*, **24**, 1239 (1956).

chromite were bright green by transmitted light.

Precautions to be Observed.—Appreciable attack of the platinum crucibles was observed when the concentration of sought compound to PbO or Bi_2O_3 was too high. Dilute solutions, such as the ratio 1:6 used, produced little or no attack. Furnace linings should be new or uncontaminated by previous runs with other solvents. The presence of certain volatile substances in the muffle have been known to cause reduction of the PbO with subsequent loss of the crucible due to the alloying of Pt and Pb.

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Halogenopentacyano Compounds of Cobalt(III)

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The new compounds $K_3Co(CN)_5Br$ and $K_3Co(CN)_5I$ are described. They may be prepared either by the action of the appropriate halogen on aqueous pentacyanocobaltate(III) ion or by that of potassium cyanide on the appropriate aqueous halogenopentamminecobaltate(III) species. Possible mechanisms are discussed.

The number of known cyano complexes of Co(III) is quite limited, in contrast to the extensive family of complex ammines. The species $Co(CN)_6^{-3}$ is, of course, well known, and the following mixed cyano complexes have been reported: $K_2Co(CN)_5(H_2O)$,[1] $KCo(CN)_4(H_2O)_2$[2] and $K_4Co(CN)_5(S_2O_3)$.[1] The existence in aqueous solution of the ion $Co(CN)_4(OH)_2^{-3}$ has been postulated,[3] but the evidence is not unambiguous. Finally, a binuclear complex containing five cyanides per cobalt appears to result from the air oxidation of $Co(CN)_5^{-3}$.[4]

No mixed halogenocyano complexes of Co(III) are known, nor, indeed, do there appear to be any known for any other central metal ion. In what follows the properties of the new compounds $K_3Co(CN)_5Br$ and $K_3Co(CN)_5I$ will be described, along with evidence for the probable existence of $K_3Co(CN)_5Cl$, and a discussion of the rather interesting reactions whereby these species may be prepared.

Experimental

Preparation of $K_3Co(CN)_5Br$ by the Ray and Dutt reaction.—[1,5] Twenty-one grams of potassium bromopentamminocobaltate(III) was added, with stirring, to an aqueous solution of 24 g. of potassium cyanide, giving a dark reddish-yellow solution which evolved ammonia copiously. Addition of alcohol to about 75% by volume gave a voluminous cream colored precipitate which was filtered off, washed with alcohol and ether, and dried in a vacuum desiccator.

The product was analyzed for potassium by the chloroplatinate method,[6] for cobalt by the α-nitroso-β-naphthol method[7] (after evaporation with hydrochloric acid to decompose the complex), and for bromide by an adaptation of a method reported by Kamm.[8] One quarter of a gram of the complex was refluxed with 35 cc. of absolute ethanol and 3.5 g. of metallic sodium was added gradually. After about two hours, the solution was cooled, and 50 cc. of water added. The solution was then acidified with nitric acid and the bromide present determined by the Volhard method. Found for K, 30.5 ± 0.4%; Co, 15.7 ± 0.1%; Br, 19.4 ± 0.05%. Calcd. for $K_3Co(CN)_5Br$: K, 30.4; Co, 15.3; Br, 20.7. Calcd., assuming 6.3% $K_2CO(CN)_5(H_2O)$ impurity: K, 30.2; Co, 15.6; Br, 19.4.

The compound is very soluble in water and insoluble in organic solvents; as with $Co(CN)_6^{-3}$, insoluble salts are formed with a number of transition metal ions. The dry potassium salt is light brown in color, and, in aqueous solution gives an absorption maximum at 393 mμ with an extinction coefficient of 163.

Rate Studies.—Qualitative rate data were obtained for the above reaction by adding aqueous potassium bromopentamminecobaltate(III) to solutions of potassium cyanide buffered to the desired *p*H by either acetate or phosphate buffer. Qualitative rates were obtained either by noting the rate of color change or, in some cases, from a spectrophotometric measurement of the optical density.

Preparations by the Reaction of Halogen with $Co(CN)_5^{-3}$.—The procedure for the preparation of the bromide was as follows. A solution of 20 g. of cobalt(II) nitrate hexahydrate in 150 cc. of water was deaerated by bubbling nitrogen through it, and cooled to *ca.* 5°. Solid potassium cyanide was then added slowly, in amount sufficient to give a clear solution (a slight excess over five cyanides per cobalt). This solution was then added rapidly to one containing a small excess of bromine, and the product was isolated by alcohol precipitation as described above. The $K_3Co(CN)_5Br$ product was analyzed for cobalt by the method of Cartledge and Nichols[9] (after sulfuric acid digestion), for potassium by a flame spectrophotometer, and for bromide, as before. *Anal.* Calcd. for $K_3Co(CN)_5Br$: K, 30.3; Co, 15.3; Br, 20.7. Found: K, 28.5; Co, 15.8; Br, 21.9. The analyses suggest the presence of an impurity such as $CoBr_2$, but no satisfactory method was found to purify the product further.

The procedure for the preparation of $K_3Co(CN)_5I$ was similar to that above, except that aqueous potassium triiodide was employed instead of bromine water. Analyses were likewise by the same procedures as above. *Anal.* Calcd. for $K_5Co(CN)_5I$; K, 27.3; Co, 13.6; I, 29.3. Found: K, 25.9; Co, 14.0; I, 29.8. The product was reddish brown in color, its solubility characteristics were similar to those of $K_3Co(CN)_5Br$, and its aqueous solution showed a shallow absorption maximum at 495 mμ, with an extinction coefficient of 95, followed by an intense band in the near ultraviolet.

The course of the reaction with aqueous chloride as oxi-

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