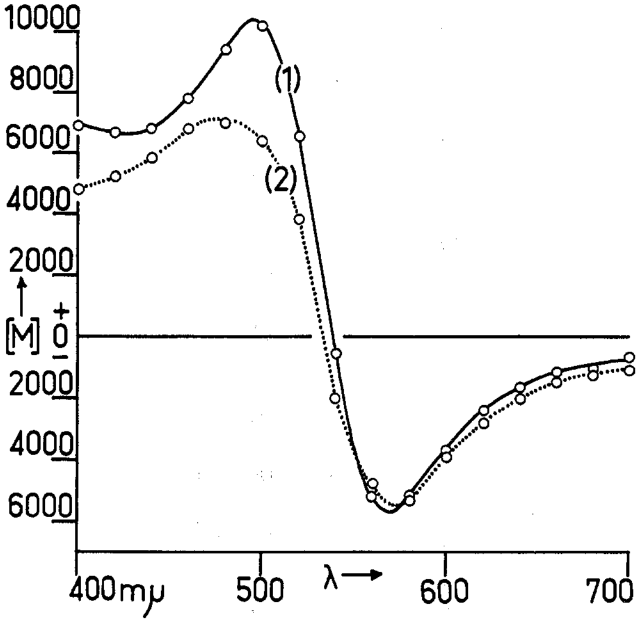

Fig. 1.—Rotatory dispersion curves: (1) L-$[Co(l\text{-}pn)_2CO_3]I$; (2) L-$[Co(en)_2CO_3]I$.

iodide was dissolved in water and acetone was added until the salt was on the point of precipitating. The solution so obtained was kept at 30° for 1 week, during which time practically all the complex iodide had separated out as orange-pink crystals. Analyses showed that this was the anhydrous iodide and the rotatory dispersion curve indicated that it was pure L-$[Co(l\text{-}pn)_2CO_3]I$.

Figure 1 shows the rotatory dispersion curve for this isomer and compares it with that for pure L-carbonatobis-(ethylenediamine)-cobalt(III) iodide. The difference is similar to that between L-$[Co(l\text{-}pn)_2C_2O_4]I$ and L-$[Co(en)_2C_2O_4]I$.[4]

The equilibrium which exists between D- and L-$[Co(l\text{-}pn)_2CO_3]^+$ ions and the lower solubility of the iodide of the levorotatory isomer in aqueous acetone enabled this stereospecific synthesis to be achieved.

This investigation indicates that the isomers obtained previously[1,2] were about 75% pure. Subsequent stereospecific reactions[5,6] might be improved by using the product of the present investigation.

Experimental

D,L-Carbonatobis-(*l*-propylenediamine)-cobalt(III) Chloride 1-Hydrate.—Carbon dioxide gas was bubbled through an aqueous solution of cobalt(II) chloride hexahydrate (40 g.) and *l*-propylenediamine (86.3 ml., 28.5% aqueous solution) was added slowly while the temperature was raised to 80°. The carbon dioxide flow then was stopped and lead(IV) oxide (30 g.) was added slowly while stirring the mixture to prevent caking. Vigorous stirring was continued for 3 hr. at 80° and the mixture was filtered while hot. Lithium carbonate (29 g.) was added to the filtrate, which was stirred at 60° for 8 hr., filtered, and evaporated in the presence of small amount of lithium carbonate (2 g.) to 250 ml., and again filtered (pH 10). Calcium chloride hexahydrate (10 g.) was added to the cooled solution, which then was stirred for 3 min. and filtered through a Whatman 542 paper. Ethanol (5 l.) was added to the filtrate and the flocculent precipitate was stirred for 5 hr., collected at the pump, washed with ethanol and then acetone, and air-dried at 70°. The filtrate was cooled in a refrigerator overnight to give further product. The total yield was 34 g. (64%); $[\alpha]_D$ −40°. *Anal.* Calcd. for $[Co(C_3H_{10}N_2)_2CO_3]Cl\cdot H_2O$: C, 26.25; H, 6.88; N, 17.50. Found: C, 26.59; H, 6.81; N, 17.45.

L-Carbonatobis-(*l*-propylenediamine)-cobalt(III) Iodide.—The above chloride (20 g.) was dissolved in a small volume of water and precipitated almost completely with excess solid sodium iodide. The crude iodide was collected at the pump, washed with acetone, and air-dried. It then was dissolved in a minimum volume of water and acetone was added until the solution was slightly cloudy. The flask was stoppered and kept at 30° for 1 week. The crystalline precipitate which formed gradually in the course of the week was filtered off and washed with acetone. It was recrystallized twice from water by adding acetone, collected at the pump, washed with acetone, and air-dried. The rotatory dispersion curve of a 0.04% solution in a 1-dm. tube was obtained using a Shimadzu manual spectrophotometer with a photoelectric polarimeter attachment. It is shown in Fig. 1 and is there compared with the curve for L-$[Co(en)_2CO_3]I$. *Anal.* Calcd. for $[Co(C_3H_{10}N_2)_2CO_3]I$: C, 21.16; H, 5.04; N, 14.10. Found: C, 21.19; H, 5.19; N, 14.09.

---

[4] T. E. MacDermott and A. M. Sargeson, *Australian J. Chem.*, in press.

[5] J. C. Bailar, Jr., C. A. Stiegman, J. H. Balthis, and E. H. Huffman, *J. Am. Chem. Soc.*, **61**, 2402 (1939).

[6] J. C. Bailar, Jr., and A. D. Gott, *ibid.*, **74**, 4820 (1952).

CONTRIBUTION FROM THE SPERRY RAND RESEARCH CENTER,
SUDBURY, MASSACHUSETTS

Preparation and Properties of Chromium Borate

BY N. C. TOMBS, W. J. CROFT, AND H. C. MATTRAW

Received February 8, 1963

Ternary compound formation in the system chromium–boron–oxygen has previously been sought without success. Keith and Roy[1] found that heating of equimolar mixtures of Cr_2O_3 and B_2O_3 at 1000° yielded only Cr_2O_3 as a crystalline phase. Prolonged heating (7 days) at 1000° caused gradual evaporation of B_2O_3. The originally fine-grained Cr_2O_3 grew into larger crystals up to 0.1 mm. in size. Earlier, Partington[2] referred to recrystallization of Cr_2O_3 by fusion with B_2O_3 and $CaCO_3$. However, no details are given concerning ratios, temperatures, or duration of heating; the $CaCO_3$ is presumably included to act as a "mineralizer."

In this Laboratory chromium borate, $CrBO_3$, has been prepared by reaction between Cr_2O_3 and B_2O_3 in molten B_2O_3 at 1100°. The crystal structure is rhombohedral. Based on a hexagonal cell the dimensions are $a_0 = 4.5775$ Å., $c_0 = 14.258$ Å.; space group $R\bar{3}c$ (D_{3d}^6). DTA studies show that decomposition to Cr_2O_3 and B_2O_3 occurs at 1220°.

A study of ABO_3-type rare earth borates by Levin,

---

[1] M. L. Keith and R. Roy, *Am. Mineralogist*, **39**, 1 (1954).

[2] J. R. Partington, "General and Inorganic Chemistry," 2nd Ed., The Macmillan Co., New York, N. Y., 1951, p. 743.

Roth, and Martin[3] included the In and Mn systems but was not extended to Cr.

Experimental

Mixtures of 30 g. of H_3BO_3 (A.R. grade), 0.3 g. of Cr_2O_3 ("Purified" grade), and 0.3 g. of $CaCO_3$ (A.R. grade) were heated cautiously in a platinum dish to dehydrate the H_3BO_3. The dish containing the anhydrous melt was then heated in a Globar furnace to the selected temperature inside a deep cylindrical mullite container which was covered by a mullite lid. After cooling, the melt was extracted by prolonged boiling in water.

Reaction for 12 hr. at 1100° gave almost complete conversion to a green crystalline material (I), having a consistent X-ray pattern different from that for Cr_2O_3. Crystals up to about 0.1 mm. on a side were obtained. The faces were well developed and not etched by the boiling water treatment. In some samples a few faint X-ray reflections were noted for Cr_2O_3 and $CaCO_3$ (calcite). The latter could be eliminated by treatment with dilute HCl.

Reaction for 12 hr. at 1175° gave a similar result, but at 900° only slight conversion to I occurred; at 1250° only Cr_2O_3 was obtained.

Subsequent experiments showed that the addition of $CaCO_3$ to the reaction mixture was not essential for the formation of I, although the reaction and crystallization rates were increased by this addition. $CaSO_4$ appeared to be of comparable effectiveness as a "mineralizer." Decrease of the H_3BO_3 content by a factor of 10 did not modify the results.

X-Ray diffraction powder data (Table I) were obtained for I using a Norelco diffractometer with Cu Kα radiation ($\lambda = 1.5405$ Å.). The reflections have been indexed in terms of a hexagonal unit cell (calcite or $NaNO_3$-type structure) with $a_0 = 4.5775$ Å., $c_0 = 14.258$ Å. The space group is R$\bar{3}$c (D_{3d}^6). Emission spectrographic analysis showed only chromium and boron as major constituents. *Anal.* Calcd.: Cr, 46.94. Found: Cr, 45.8. Using the stoichiometry $CrBO_3$ and six formula weights per hexagonal unit cell (from the $NaNO_3$ structure), the calculated density is 4.270 g./cc. This compares favorably with the experimental density 4.2 g./cc. determined with a Beckman air pycnometer.

Index of refraction measurements on I using the Na D line were unsuccessful because of the intense green color of the crystals. Using a mercury source with a green filter a value greater than 2.0 was indicated. This rather high value is consistent with calculations based on refraction data for Cr_2O_3 and B_2O_3.

Differential thermal analysis experiments on I showed an endothermic peak at 1220° (heating). This was irreversible. X-Ray examination of the material after cooling showed that Cr_2O_3 was the only crystalline phase.

Discussion

The present results show that, below 1220°, Cr_2O_3 and B_2O_3 react in a melt containing excess B_2O_3 to form a stable compound (I) identified as chromium borate, $CrBO_3$. Previous failure to obtain this simple compound can be attributed in part to ready volatilization of B_2O_3 near 1000°. This will rapidly deplete the B_2O_3 content of any near-equimolar mixture of Cr_2O_3 and B_2O_3. The decomposition of $CrBO_3$ at 1220° also limits the temperature range over which it might have been obtained. Even below 1220° the vapor pressure of B_2O_3 over $CrBO_3$ at high temperatures may be appreciable. At room temperature $CrBO_3$ is stable in air and unaffected by boiling water or by most acids. Decomposition occurs in fused alkali, as might be expected.

TABLE I
CALCULATED AND OBSERVED *d*-SPACINGS AND OBSERVED INTENSITIES FOR $CrBO_3$

hkl	*I* obsd.	*d* obsd., Å.	*d* calcd., Å.
012	92	3.46	3.464
104	100	2.651	2.651
110	19	2.288	2.288
113	42	2.062	2.062
202	27	1.909	1.909
024	17	1.732	1.732
116	33	1.648	1.649
018	16	1.625	1.626
122	18	1.466	1.466
214	14	1.381	1.381
1·0·10	3	1.342	1.342
208	7	1.325	1.325
300	20	1.3212	1.3214
119	4	1.3026	1.3026
00·12	3	1.1882	1.1881
0·2·10	4	1.1574	1.1574
128	6	1.1469	1.1468
220	6	1.1443	1.1443
312	4	1.0866	1.0866
1·1·12	3	1.0546	1.0545
134	8	1.0506	1.0506
2·1·10	4	1.0329	1.0328
226	6	1.0310	1.0310
404	5	0.9548	0.9548
318	6	.9356	.9357
2·0·14	2	.9058	.9059
232	5	.9019	.9021
3·0·12	8	.8833	.8835
324	6	.8811	.8812
1·0·16	2	.8692	.8694

The occurrence of $CrBO_3$ as a hexagonal calcite-type structure is consistent with the structure-type boundaries, in relation to ionic radius, reported for borates by Levin, Roth, and Martin.[3]

Acknowledgment.—The assistance of J. R. Carter and J. F. Fitzgerald is gratefully acknowledged.

---

[3] E. M. Levin, R. S. Roth, and J. B. Martin, *Am. Mineralogist*, **46**, 1030 (1961).

CONTRIBUTION FROM THE CRYSTALLOGRAPHY LABORATORY,
UNIVERSITY OF PITTSBURGH, PITTSBURGH, 13 PENNSYLVANIA

Single Crystal Studies on Some Clathrates of Tetra-(4-methylpyridine)-nickel(II) and Cobalt Dithiocyanates[1]

BY D. BELITSKUS, G. A. JEFFREY, R. K. MCMULLAN, AND N. C. STEPHENSON[2]

Received February 15, 1963

This note reports and discusses the crystal data from single crystals of some clathrate compounds of tetra-(4-methyl pyridine)-nickel(II) and cobalt(II) dithiocyanates previously described by Hart and Smith.[3] The compounds were prepared as described in their

---

[1] This research was aided by a grant from the Office of Saline Water, U. S. Dept. of the Interior.

[2] On leave from the University of New South Wales, Australia.