compounds. The relationship with neodymium is particularly evident in view of the structural similarity observed between Pr(Nd)Cl$_{2.32}$ and NdCl$_{2.37}$, phases substantially identical within the precision of the separate and different determinations of their composition. Although the liquid phase behavior of lanthanum and cerium is more difficult to assess, it already has been noted that the cryoscopic data for dilute solutions of La, Ce, and Nd are quite consistent with solution as M^{2+}.[6] Similarly, in the present system the cryscopic number n of 2.9 calculated from the $PrCl_3$ liquidus curve and the calorimetric heat of fusion[10] appears compatible with the formation of Pr^{2+} ($n = 3.0$) but not Pr^+ ($n = 1.5$) or Pr^0 ($n = 1.0$). (An ideal solution of metal as Pr^{3+} plus anion-like electrons is in principle indistinguishable from the Pr^{2+} solute although it is considered less plausible.) It is interesting to note that the electronic conductivity observed for these metal solutions decreases from lanthanum to the salt-like behavior of neodymium as the presumed M^{2+} stability increases; in all cases the temperature coefficient of conductivity is apparently positive.[6,11]

The present chloride PrCl$_{2.31}$ may be compared to the formation of the stable PrBr$_{2.38}$ in the $PrBr_3$–Pr system[7] and the compound PrI$_{2.00}$ as well as the congruently melting PrI$_{2.50}$ in PrI_3–Pr.[12] A notable difference exists among these phases in their electrical properties, however. The diiodide is apparently metallic ($Pr^{3+}(I^-)_2e^-$)[12] and, although the corresponding property of PrI$_{2.50}$ is unknown, PrBr$_{2.38}$ exhibits a moderate conductivity suggestive of semiconduction.[7] On the other hand, the stabilized Pr(Nd)Cl$_{2.31}$ has megohm resistances typical of an ionic salt. In view of the observed properties it thus seems proper to consider PrCl$_{2.31}$ as a typical, reduced salt with Pr^{2+} and Pr^{3+} ions in the (unknown) lattice in roughly a 2:1 proportion. The compound has the lowest stability with respect to disproportionation of any phase identified to date in metal–metal halide systems.

The conclusions regarding the existence of Pr^{2+} in the liquid as well as in the solid state appear to be supported by the recent studies of Novikov and Polyachenok[13] of the vapor pressure of $PrCl_3$ above $PrCl_3$ + Pr solutions. At 1180° the lowering of the vapor pressure of $PrCl_3$ is proportional to the concentration of metal up to saturation (24.5%) and extrapolates to the composition $PrCl_2$ for zero pressure of $PrCl_3$. The system thus appears to be a reasonably ideal mixture of $PrCl_3$ with the non-volatile $PrCl_2$. The thermal analysis data given in the same paper are not consistent, however, with the present results. In addition to the $PrCl_3$ liquidus, somewhat higher than reported here, thermal arrests at 645 *and* 665° were observed for mixtures containing from about 8 to 32% Pr. The higher halt was attributed to the separation of solid $PrCl_3$ and $PrCl_2$ (or their solid solutions) from the melt, and the lower, to the possible decomposition of the latter into $PrCl_3$ and Pr. The invariant temperatures reported are thus roughly as found here, but with the higher taken to be the eutectic (at 16.7% Pr). It is difficult to reconcile their observation of the 665° halt for mixtures containing less metal than the eutectic composition with the peritectic separation of PrCl$_{2.31}$ that properly is found only beyond the eutectic.

The observation of a f.c.c. phase for mixtures of about equal amounts of neodymium and praseodymium is the same as was found earlier with cerium in the reduced neodymium chlorides. On the basis of evidence previously cited[5] the present behavior presumably also can be interpreted as the interstitial substitution of Cl^- together with M^{3+} for M^{2+} in the cation sites of the (hypothetical) fluorite structure of MCl_2 to give the limiting composition MCl$_{2.25}$ ($3MCl_2 \cdot MCl_3$). No evidence for a f.c.c. phase $NdCl_{2+x}$ ($0.0 < x < 0.25$) has been found in further investigation of these compositions in the neodymium system. It is not clear why praseodymium and cerium ions, although only a few hundredths of an Ångstrom larger than those of neodymium, should be apparently necessary for and so surprisingly effective in the stabilization of the f.c.c. structure.

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The Stereospecific Preparation of L-Carbonatobis(*l*-propylenediamine)-cobalt(III) Iodide

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Bailar and co-workers have shown[2] that under different conditions of preparation the carbonatobis-(*l*-propylenediamine)-cobalt(III) ion may be obtained with either a positive or a negative rotation at the sodium D line, and that these two forms are interconvertible. A direct method of synthesis of carbonatobis-(*l*-propylenediamine)-cobalt(III) based on the lead-(IV) oxide oxidation method described for the corresponding oxalato ethylenediamine compound[3] has enabled this complex to be prepared on a large scale, and reinvestigated. The pink chloride was obtained analytically pure by precipitation from the reaction mixture with ethanol and was converted to the iodide by adding sodium iodide to an aqueous solution. This

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[10] ΔH_{fus} = 12.1 kcal. mole^{-1}: A. S. Dworkin and M. A. Bredig, *J. Phys. Chem.*, **67**, 697 (1963).

[11] A. S. Dworkin, H. R. Bronstein, and M. A. Bredig, *ibid.*, **66**, 1201 (1962).

[12] J. D. Corbett, L. F. Druding, W. J. Burkhard, and C. B. Lindahl, *Discussions Faraday Soc.*, **32**, 79 (1961).

[13] G. I. Novikov and O. G. Polyachenok, *Zh. Neorgan. Khim.*, **7**, 1209 (1962).

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[2] (a) J. C. Bailar, Jr., and J. P. McReynolds, *J. Am. Chem. Soc.*, **61**, 3199 (1939); (b) J. C. Bailar, Jr., and S. M. Martinette, *ibid.*, **74**, 1054 (1952).

[3] F. P. Dwyer, I. K. Reid, and F. L. Garvan, *ibid.*, **83**, 1285 (1961).

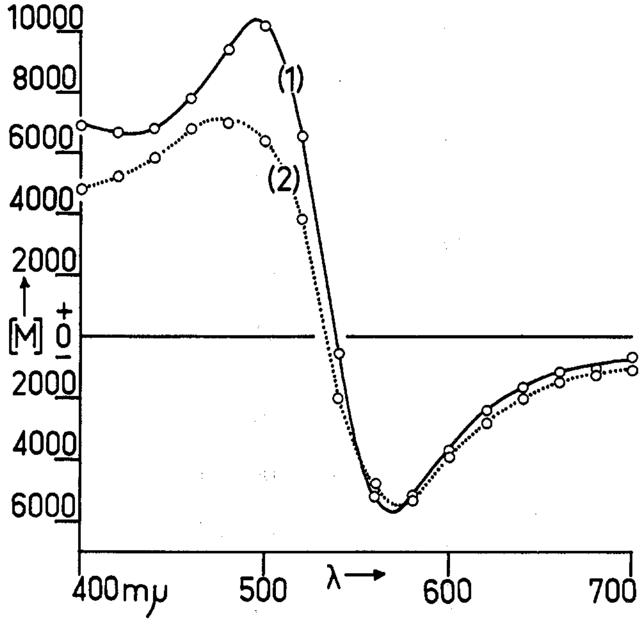

Fig. 1.—Rotatory dispersion curves: (1) L-[Co(l-pn)$_2$CO$_3$]I; (2) L-[Co(en)$_2$CO$_3$]I.

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-pn)$_2$CO$_3$]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-pn)$_2$C$_2$O$_4$]I and L-[Co(en)$_2$C$_2$O$_4$]I.[4]

The equilibrium which exists between D- and L-[Co(l-pn)$_2$CO$_3$]$^+$ 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$_3$H$_{10}$N$_2$)$_2$CO$_3$]Cl·H$_2$O: 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)$_2$CO$_3$]I. *Anal.* Calcd. for [Co(C$_3$H$_{10}$N$_2$)$_2$CO$_3$]I: C, 21.16; H, 5.04; N, 14.10. Found: C, 21.19; H, 5.19; N, 14.09.

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[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).

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Preparation and Properties of Chromium Borate

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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$_2$O$_3$ and B$_2$O$_3$ at 1000° yielded only Cr$_2$O$_3$ as a crystalline phase. Prolonged heating (7 days) at 1000° caused gradual evaporation of B$_2$O$_3$. The originally fine-grained Cr$_2$O$_3$ grew into larger crystals up to 0.1 mm. in size. Earlier, Partington[2] referred to recrystallization of Cr$_2$O$_3$ by fusion with B$_2$O$_3$ 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$_2$O$_3$ and B$_2$O$_3$ in molten B$_2$O$_3$ 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$_2$O$_3$ and B$_2$O$_3$ occurs at 1220°.

A study of ABO$_3$-type rare earth borates by Levin,

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[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.