$$[Os(NH_3)_6]Br_3 + 3K^+ + 3e^- \longrightarrow [Os(NH_3)_6] + 3K^+ + 3Br^- \quad (2)$$

in liquid ammonia at −33.5°. Both $Pt(NH_3)_4$ and $Os(NH_3)_6$ are too unstable for use in experiments designed to determine whether these species involve metal–hydrogen bonds; such studies, however, are in progress using the relatively more stable $Ir(NH_3)_5$.

An improved procedure for the synthesis of hexaammineosmium(III) bromide also is described.

### Experimental

**Materials.**—Ammonium hexabromoösmate(IV) was prepared by the method of Dwyer and Gibson.[4]

For the preparation of hexaammineosmium(III) bromide, 4.6210 g. of $(NH_4)_2OsBr_6$ was placed in a Faraday tube and maintained at $10^{-3}$ mm. for 12 hr. to ensure complete dryness. Forty ml. of anhydrous $NH_3$ was condensed on the solid and the tube was sealed and allowed to stand for 28 days at 25°. Thereafter, the insoluble product was washed four times with 40-ml. portions of $NH_3$, the tube was cooled to −78°, opened, and the solvent evaporated. The brown $NH_3$-insoluble product was dissolved in 40 ml. of $H_2O$ and the resulting solution was passed through a column (18 in. × 15 mm. i.d.) of freshly activated $Al_2O_3$. The column was washed with $H_2O$ until the washings failed to produce a white precipitate when added to $NH_4Br$-saturated $C_2H_5OH$; brown impurities remained on the column. When excess $NH_4Br$-saturated $C_2H_5OH$ was added to the eluate, 1.0990 g. [31.6% based on $(NH_4)_2OsBr_6$] of white solid precipitated. *Anal.* Calcd. for $[Os(NH_3)_6]Br_3$: Os, 35.8. Found: Os, 35.8. X-Ray diffraction data for this product were essentially identical with those reported earlier[5] for $[Os(NH_3)_6]Br_3$.

**Preliminary Experiments.**—To establish that $[Os(NH_3)_6]Br_3$ does not ammonolyze, a 0.2072-g. sample was dissolved in 125 ml. of liquid $NH_3$ and allowed to stand for 4 hr., after which the solvent was evaporated. The dry residue gave an X-ray diffraction pattern identical with that of the original bromide; there were no lines attributable to $NH_4Br$.

Using equipment and procedures described elsewhere[6,7] a solution of 0.2958 g. of $[Os(NH_3)_6]Br_3$ in 135 ml. of liquid $NH_3$ was titrated potentiometrically with a 0.0912 *M* solution of K in $NH_3$ at −33.5° over a period of 14 hr. Significant changes in potential occurred upon addition of 1, 2, and 3 molar equivalents of the titrant. The solid phase that began to separate during the addition of the latter part of the first equivalent and that was present upon addition of 2 equivalents was a voluminous bright yellow precipitate; that present after addition of 3 equivalents was more dense and dark brown. Water-insoluble gases were not evolved during the course of the titration. The yellow-brown supernatant solution was removed by filtration and the brown solid was washed three times with 100-ml. portions of $NH_3$; analysis of the residue from the combined supernatant solution and washings accounted for 94.3% of the Br used as $[Os(NH_3)_6]Br_3$. The brown $NH_3$-insoluble product was stable at −33.5° but decomposed when warmed to 25° to form (*only*) $NH_3$ and Os; the latter was identified by X-ray diffraction data.

**Isolation of $[Os(NH_3)_6]Br$.**—Using equipment and procedures described earlier,[8] 0.3600 g. of $[Os(NH_3)_6]Br_3$ in 130 ml. of liquid $NH_3$ was reduced by addition of 2 molar equivalents of K in $NH_3$ (13.8 ml. of 0.0905 *M* solution). The resulting bright yellow precipitate was separated by filtration and washed three times with 30-ml. portions of $NH_3$; analysis of the residue from the combined filtrate and washings accounted for 63.3% of the Br used as $[Os(NH_3)_6]Br_3$.

The yellow solid was warmed to room temperature, dried under reduced pressure for 4 hr., and removed from the reactor in an anhydrous $O_2$-free atmosphere. *Anal.* Calcd. for $[Os(NH_3)_6]$-Br: Os, 51.1; Br, 21.5. Found: Os, 50.5; Br, 22.0. As expected, this product was paramagnetic (1.5 B.M.). An X-ray diffraction pattern[9] led to the following *d*-spacings (Å.) (relative intensities in parentheses): 6.10 (0.75), 5.16 (0.20), 3.74 (1.00), 3.14 (0.05), 2.72 (0.07), 2.59 (0.15), 2.15 (0.05). Upon exposure to the atmosphere or water this product decomposed slowly.

**Establishment of the Composition of $[Os(NH_3)_6]$.**—Since the separation of KBr from the Os-containing product of reaction 2 had been demonstrated and because this product was too unstable for analysis at 25°, it was necessary and possible otherwise to establish its composition without separation from KBr; this was done as follows.

In a typical experiment, 0.4534 g. of $[Os(NH_3)_6]Br_3$ in 130 ml. of liquid $NH_3$ was treated with 3 molar equivalents of K in $NH_3$ (0.111 *M* solution). A connection was made from the top of the reactor[8] to a trap inside a dewar flask. The trap was cooled by adding liquid nitrogen at a rate such that the solvent distilled from the reactor at a smooth controlled rate. When all of the *liquid* $NH_3$ was removed, the trap was maintained at liquid nitrogen temperature for 1 hr., the temperature of the reactor was lowered to −78°, and the pressure therein was reduced to $10^{-3}$ mm. for 18 hr. The brown solid showed no evidence of change during these operations. Thereafter, the reactor was connected to a gas collection system (including a Toepler pump) and the brown solid was decomposed by allowing it to warm to 25° followed by heating it at 100° for 1 hr. The solid turned black and $4.85 \times 10^{-3}$ mole of $NH_3$ gas was collected; this corresponds to 5.71 moles of $NH_3$/mole of Os originally introduced as $[Os(NH_3)_6]Br_3$. The X-ray data obtained using a sample of the black residue showed the presence of only Os and KBr.

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# Rare Earth Metal–Metal Halide Systems. VI. Praseodymium Chloride[1]

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The reaction of praseodymium with liquid $PrCl_3$ is of interest in relation to the behavior of the neighboring rare earth metal–metal halide systems. Lanthanum and cerium show only the phenomenon of solution in their respective molten trichlorides with no intermediate solid phases. The solubility in $LaCl_3$ has been reported to be 9 (mole) % at the eutectic (826°) and 11% at 920°,[3] and in $CeCl_3$, 9.3% at the monotectic (777°)

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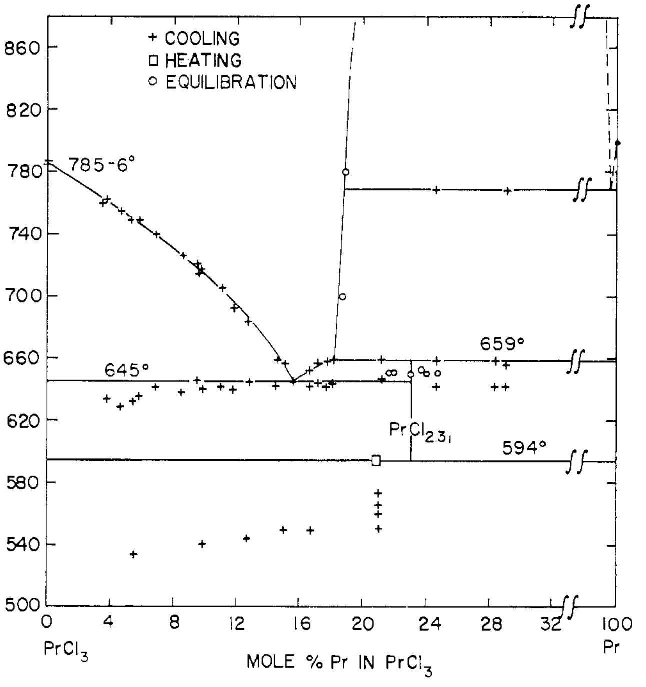

Fig. 1.—The system $PrCl_3$–Pr.

and 9.6% at 950°.[4] A considerably greater reaction takes place in the $NdCl_3$–Nd system, where the compound $NdCl_2$ separates at 841° from the limiting solution of 30.5% Nd in liquid $NdCl_3$, and the intermediate $NdCl_{2.37}$ and $NdCl_{2.27}$ are also stable at lower temperatures.[5] The trichloride liquidus curves obtained on solution of metal in these three cases are all consistent with the formation of $M^{2+}$ in solution, as opposed to $M^+$ or $M^0$,[6] while the stability of $Ce^{2+}$ in the solid state had been specifically supported by its substitution in reduced neodymium chlorides.[5]

## Experimental

The pure metals, supplied through the courtesy of Drs. F. H Spedding and A. H. Daane, had typical analyses of O, 500–700 C, 100; N, 100; Ca, <200; total other rare earth metals, <500 p.p.m. The preparation of $PrCl_3$ and the apparatus and techniques for phase study and analyses were as previously described.[5,7] Ta and Mo were employed as the container material for all studies of the system. Vacuum sublimed $PrCl_3$ was used for studies of the $PrCl_3$ liquidus curve and for equilibrations to establish the composition of the intermediate solid phase. The latter experiments were carried out for 18 to 30 hr. with continuous, proportioning temperature control. The metal and salts were stored in evacuated containers, and all transfers were carried out in an argon-flushed drybox.

## Results

The $PrCl_3$–Pr system exhibits the formation of the slightly-stable intermediate compound $PrCl_{2.31}$, as characterized by the equilibrium phase diagram given in Fig. 1. The compound melts peritectically at 659° to Pr(s) and the solution of 18.3% Pr in $PrCl_3$, only slightly different from the eutectic at 645° and 15.7% Pr. The composition of the new phase was established by equilibration of salt with excess metal between the 645 and 659° points required by the phase relationships for a practical rate of formation. The composition results had a range of ±0.08 in Cl–Pr, somewhat greater than obtained in other systems, with a standard deviation of ±0.02.

An earlier, preliminary report[8] of the absence of an intermediate phase in this system was based on the fact that diffractions characteristic of only the original components are observed in X-ray powder patterns taken of mixtures that have been equilibrated at 800 to 900° and quenched. Subsequent improvements in instrumentation not only resolved the peritectic and eutectic arrests, indicating a new phase was formed, but also showed that the $PrCl_{2.31}$ compound disproportionates into $PrCl_3$ and Pr about 65° below its melting point. On cooling, this rather sluggish reaction is observed thermally at 530 to 550° under normal conditions and as high as about 574° at slower cooling rates, while reaction of the intimate mixture of $PrCl_3$ and Pr on heating is observed at 594°. The recombination is accomplished in less than 10 min. at 595° and not at all in 8 hr. at 590°, as evidenced by thermal analysis on cooling. The equilibrium temperature is therefore taken to be near 594°, Fig. 1.

A significant solubility of salt in the solid metal is also to be noted according to the phase results. The b.c.c. → hex. transition found at 798° on cooling the pure metal[9] occurs at 769° in the presence of $PrCl_3$.

In order to establish whether the intermediate $PrCl_{2.31}$ has any structural relationship to the known neodymium phases, small amounts of neodymium metal were added to the praseodymium system. Three mole % Nd in the salt phase proved sufficient to stabilize the new phase. Equilibrations with excess metal (alloy) as before gave a composition of $Pr(Nd)Cl_{2.32 \pm 0.024}$, substantially the same as in the binary system, indicating that the phase obtained is apparently the same as encountered in the binary system only at higher temperatures. The neodymium-stabilized product gives the same powder pattern as derived earlier[5] for $NdCl_{2.37 \pm 0.02}$. With a Nd:Pr ratio of from about 0.6 to at least 1 in the salt phase, the powder pattern of the product ($\sim MCl_{2.15}$) is that of a f.c.c. structure, $a_0$ = 7.00 Å., as found earlier for the cerium–neodymium system.[5]

## Discussion

The character of the praseodymium system appears to be properly intermediate to the solution behavior that is found with lanthanum and cerium and the more stable, reduced compounds that occur with neodymium. The trend suggests that for the lighter rare earth elements there is a more or less regular increase in stability of the M(II) halides with increasing atomic number toward the better known Sm(II) and Eu(II)

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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 carbonato-bis-(*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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