Fig. 4.—Plots of $(R_2 + R'')/[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{H}_2\text{O})^+]$ vs. chloride concentration. Indicated $\Delta H^* = 20.3$ kcal., $\Delta S^* = -11$ e. u.

values of the parameter less than 1.0. In Fig. 4 has been plotted the quantity $(R_2 + R'')/[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{H}_2\text{O})^+]$ vs. $[\text{Cl}^-]$ for all cases in which it was calculated. Although the values do increase somewhat with $[\text{Cl}^-]$, it was felt that the increase was not significant in view of the uncertainty in the parameter at the higher chloride concentration. It has been concluded, therefore, that the reaction rate sum $(R_2 + R'')$ is substantially zero order in chloride. The weighted averages for the indicated first order rate constants $(k_2 + k'')$, together with

values for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ have been included with the data in Fig. 4.

It has not been possible to separate the individual reaction rates R_2 and R''. Since reaction 12, with the rate R'', is chloride independent and is not a solvation process, it presumably would have to proceed by a dissociative mechanism. It is possible that the entire exchange is carried by the acid hydrolysis, i.e., $k'' \ll k_2$.

In the experiments which have been completed with the systems of $[\text{PtCl}_4]^=$, $[\text{Pt}(\text{NH}_3)\text{Cl}_3]^-$ and cis-$[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$, it has been found that the acid hydrolysis accounts completely for the exchange of the species, $[\text{PtCl}_4]^=$ and cis-$[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$. All the other exchange processes in these systems are also chloride independent. In addition, all these first order reaction rate constants lie in the narrow range of 2.5-10×10^{-5} sec.$^{-1}$, and all indicate rather similar entropies and energies of activation.

Basolo and Pearson[11] have indicated that the similarity of reaction rates for complex species whose charges ranged from -2 to 1 indicate that a simple dissociative mechanism to a coordination of 3 does not occur in the substitution reaction. The present experiments appear to support such a conclusion. It does appear likely that all the chloride exchange processes in these three systems occurs by the acid hydrolysis, and the chloride ion cannot compete with the solvent in the replacement of a chloride ion under the concentration conditions which have been studied. Apparently, the water ligand can be replaced rapidly by chloride or by many other substituting groups so the rate of the acid hydrolysis controls the rate of many substitution reactions, including the rate of base hydrolysis.

(11) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 194.

Lower Oxidation States of the Lanthanides. Neodymium(II) Chloride and Iodide[1]

By LEONARD F. DRUDING AND JOHN D. CORBETT

Investigation of the salt-rich portions of the Nd–NdCl₃ and Nd–NdI₃ phase diagrams establishes the existence of the incongruently melting NdCl₂.₃₇ (680°), NdCl₂.₂₇ (702°) and NdCl₂.₀₀ (841°) and the congruently melting NdI₁.₉₅ (562°) Neodymium(II) chloride is isomorphous with SmCl₂ and NdI₁.₉₅ with SmBr₂. The composition and powder patterns of solid solutions of cerium in NdCl₂.₃₇ suggest substitution of a reduced cerium species, presumably Ce^{+2}, therein. The formation of a face-centered-cubic (Nd, Ce)Cl₂.₂₀ phase at higher Nd/Ce ratios is considered in terms of anion substitution in the body center of the fluorite structure. A new method is given for the preparation of the pure rare earth metal trichlorides and iodides by the reaction of HCl or I₂ with the metals in molybdenum or tungsten containers, respectively.

Introduction

The solubilities of certain metals in their molten salts have evoked considerable interest in recent years as the chemist has turned to the study of reactions at higher temperatures. Recent investigations have centered upon the alkali[2-4]

(1) Presented at the 138th meeting of the American Chemical Society, New York, N. Y., Sept. 14, 1960. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

(2) M. A. Bredig, H. R. Bronstein and W. T. Smith, Jr., *J. Am. Chem. Soc.*, **77**, 1454 (1955).

(3) J. W. Johnson and M. A. Bredig, *J. Phys. Chem.*, **62**, 604 (1958).

alkaline earth[5-7] and post-transition[8-10] metal metal halide systems. Although the phenomenon

(4) M. A. Bredig and H. R. Bronstein, *ibid.*, **64**, 64 (1960).

(5) D. Cubicciotti and C. D. Thurmond, *J. Am Chem. Soc.*, **71**, 2149 (1949).

(6) H. Schäfer and A. Niklas, *Angew. Chem.*, **64**, 611 (1952).

(7) P. S. Rogers, J. W. Tomlinson and F. D. Richardson, *Trans. Met. Soc. AIME*, in press.

(8) J. D. Corbett and S. v. Winbush, *J. Am. Chem. Soc.*, **77**, 3964 (1955).

(9) J. D. Corbett, S. v. Winbush and F. C. Albers, *ibid.*, **79**, 3020 (1957).

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

has been known for over a century, a completely satisfactory interpretation of this behavior is not yet available. At least for the post-transition metals, present evidence indicates that one of the most attractive explanations is the formation of a slightly-stable, lower oxidation state in the melt that disproportionates to metal and the normal salt upon solidification[9,10]

Studies of the interactions of the lanthanide metals with their molten halides have thus far been limited to the cerium and lanthanum chloride systems. For Ce–CeCl₃ Mellors and Senderoff[11] report a solubility of 9 mole per cent in the liquid salt, essentially invariant from 777° (monotectic) to 950°. Data from concentration cell measurements on this system were interpreted in terms of the formation of Ce^+ as the solute,[12] and the equilibrium $Ce^+ = Ce^{+3} + 2e^-$ subsequently applied to the explanation of conductivity data[13] However, it is now doubtful that either the emf. or the conductivity data are valid as the alumina crucibles used in these studies, and even large crystals of synthetic sapphire, have been shown to react with the cerium solutions to form CeOCl and Al or Ce–Al alloys.[14] The recent work of Keneshea and Cubicciotti[15] indicates that solubility of lanthanum in its liquid trichloride is comparable to that found in the cerium system, being 9% at 826°, the eutectic, and 11% at 914°, the monotectic temperature.

Varying degrees of metal–metal halide interactions might be expected with the other lanthanides. Knowledge of oxidation states lower than the normal three has been limited to those of Sm(II), Eu(II) and Yb(II), plus the recent characterization of Tm(II) as the iodide by Asprey and Kruse.[16] Although the monosulfides, -selenides and -tellurides have been reported for the lighter lanthanons,[17-19] physical properties indicate that these are probably better formulated as $(M^{+3}e^-Ch^=)$ rather than true divalent compounds.[20] Although there is no good evidence for a lower oxidation state for neodymium in water[21,22] or in liquid ammonia,[23] Brewer, et al.,[24] have estimated that Nd and Pm should have stable, solid dihalides while PrCl₂ should be of borderline stability.

A preliminary report on the investigation of the

(11) G. W. Mellors and S. Senderoff, J. Phys. Chem., **63**, 1110 (1959).

(12) S. Senderoff and G. W. Mellors, J. Electrochem. Soc., **105**, 224 (1958).

(13) G. W. Mellors and S. Senderoff, J. Phys. Chem., **64**, 294 (1960).

(14) H. R. Bronstein, A. S. Dworkin and M. A. Bredig, ibid., **64**, 1344 (1960).

(15) F. H. Keneshea, Jr., and D. Cubicciotti, J. Chem. Eng. Data, in press (1961).

(16) L. B. Asprey and F. H. Kruse, J. Inorg. Nuclear Chem., **13**, 32 (1960).

(17) A. Iandelli, Gazz. chim. Ital., **85**, 881 (1955).

(18) M. Picon and M. Patrie, Compt. rend., **242**, 1321 (1956).

(19) M. Picon and J. Flahout, ibid., **243**, 2074 (1956).

(20) E. D. Eastman, L. Brewer, L. A. Bromley, P. W. Gilles and N. L. Lofgren, J. Am. Chem. Soc., **72**, 2248 (1950).

(21) E. Estee and G. Glocker, ibid., **70**, 1344 (1948).

(22) H. Laitinen and E. Blodgett, ibid., **71**, 2260 (1949).

(23) P. S. Gentile, Ph.D. Thesis, Univ. of Texas, 1955.

(24) L. Brewer, L. A. Bromley, P. W. Gilles and N. L. Lofgren, "The Chemistry and Metallurgy of Miscellaneous Materials—Thermodynamics," L. L. Quill, Ed., NNES IV-19B, McGraw-Hill Book Co., New York, N. Y., 1950, paper 6.
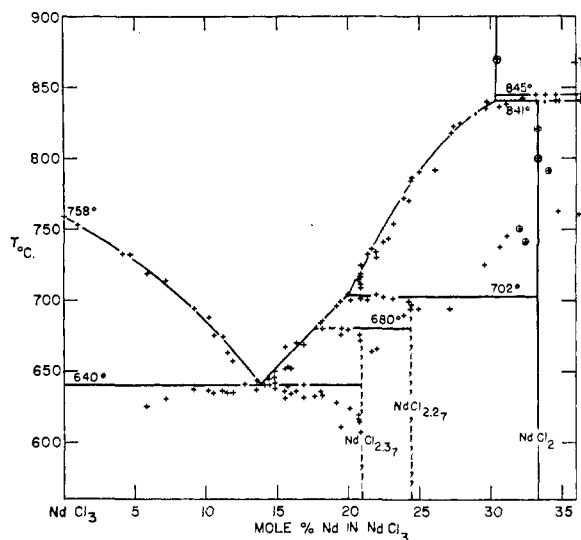
Fig. 1.—The system NdCl₃–NdCl₂: thermal analysis, +; equilibration, ⊕.

neodymium chloride and iodide systems in this Laboratory has indicated that the neodymium (II) halides are indeed stable[25]; the final results of this study follow.

Results and Discussion

The Nd–NdCl₃ System.—The initial experiments on this system indicated that in addition to the NdCl₂ there was also an intermediate chloride near NdCl₂.₃. More careful investigation, as detailed by the phase diagram in Fig. 1, shows the existence of two intermediate chlorides. The pertinent data on the neodymium chlorides are summarized in Table I; only the trichloride has a congruent melting point. The structure of NdCl₂, as determined from X-ray powder patterns, is the same as that reported by Döll and Klemm[26] for SmCl₂ and EuCl₂, namely, the orthorhombic PbCl₂ structure. The lattice constants are 4.50, 7.59 and 9.06 Å., compared to 4.48, 7.51 and 8.95 Å. remeasured for SmCl₂.

TABLE I

CHLORIDES OF NEODYMIUM

Cl/Nd	Mole % Nd in NdCl₃	M.p., °C.	Color
3.00	0	758	Rose-violet
2.37 ± 0.02	21.0 ± 0.7	680 ± 3	Black
2.27 ± 0.02	24.3 ± 0.7	702 ± 2	Black
2.00	33.3	841	Shiny black (dark green when finely ground)

The limit of solubility of neodymium in its molten trichloride was determined to be 30.5 mole per cent at 870° by equilibration and rapid quenching of samples and 30.7 mole per cent by extrapolation of the phase diagram. Equilibration of the salt phase with excess metal just below the peritectic temperature (841°) establishes the composition of the lowest chloride at $NdCl_{2.00 \pm 0.01}$.

(25) L. F. Druding and J. D. Corbett, J. Am. Chem. Soc., **81**, 5512 (1959).

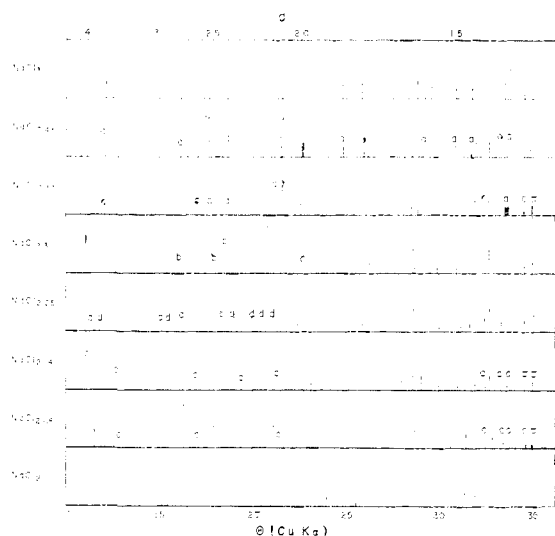(26) W. Döll and W. Klemm, Z. anorg. allgem. Chem., **241**, 392 (1939).

Fig. 2.—Comparison of powder pattern data for neodymium chlorides; minor components are designated by a, $NdCl_3$; b, $NdCl_{2.37}$; c, $NdCl_{2.27}$; d, $NdCl_2$.

In this region, the transition temperature of the metal, 868°,[27] 860° obsd., is depressed to 845°, evidently due to solid solution of salt in the metal. In addition, a small but sharp thermal halt is now found at 760–767°. This becomes more pronounced after the sample has been equilibrated below 841°, suggesting some interaction between the metal and the salt phase. A cooling curve of a 6 to 7 g. sample of pure metal showed only its freezing and transition points, yet on the addition of about 10% $NdCl_3$, the transition temperature (851°), the incongruent melting point of $NdCl_2$ and the unexplained halt at 760–767° were observed, the latter now being more pronounced than the $NdCl_2$ arrest. Analysis and powder patterns of salt samples equilibrated with excess metal above and below this temperature and then quenched gave no indication of reduction below $NdCl_{2.00}$ or of the formation of a new phase. It is not certain whether this effect is due to an induced transformation in the metal, in $NdCl_2$, or some other phase stable only at higher temperatures.

The composition of the two intermediate chlorides proved most difficult to establish. The heat effect at 680° is very small and, in fact, was overlooked in most of the early runs. Because of slow attainment of equilibrium in this region of the phase diagram and because of the slight thermal effect associated with the precipitation of these compounds, X-ray powder techniques were used to establish their composition. A condensed summary of these results is given in Fig. 2. All samples were equilibrated for at least 3 hr. at 670–675° with the exception of the $NdCl_{2.14}$ and $NdCl_{2.08}$, which were held at 690°, and the $NdCl_2$ sample, which is an average of several patterns. In each pattern, those lines considered to be *minor* constituents are marked as follows: $a = NdCl_3$, $b = NdCl_{2.37}$, $c = NdCl_{2.27}$ and $d = NdCl_2$. As the chloride content increases from $NdCl_2$, the $NdCl_2$ lines become weaker until only a few very faint

(27) F. H. Spedding and A. H. Daane, *Metallurgical Reviews*, **5**, 297 (1960).

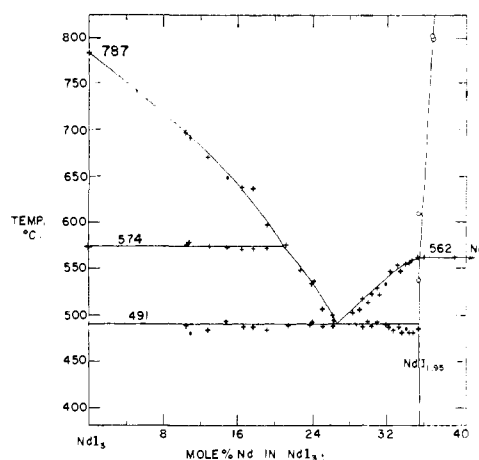Fig. 3.—The system NdI_3–$NdI_{1.95}$: thermal analysis, +; equilibration, O.

lines remain at $NdCl_{2.25}$. At this point, one or two very faint lines of the next higher phase are possibly present. In $NdCl_{2.31}$, no $NdCl_2$ lines are detectable, while several lines of the next phase are definitely present. (It is unfortunate that some of the strong lines for all of the neodymium chlorides fall in roughly the same area, making this sorting process difficult.) The $NdCl_{2.37}$ pattern shows minor lines of both $NdCl_3$ and $NdCl_{2.27}$ in about equal strength, while the $NdCl_{2.43}$ pattern shows definite evidence of only a $NdCl_3$ impurity. The fact that the $NdCl_{2.37}$ pattern shows the presence of three phases, in violation of the phase rule, indicates the difficulties of reaching true equilibrium in this system. On the basis of these observations, it appears that the two intermediate chlorides can be assigned compositions of about $NdCl_{2.37}$ and $NdCl_{2.27}$, each ± 0.02 in Cl/Nd. Thermal analysis indicates that the 640° eutectic vanishes about $NdCl_{2.37}$, but this evidence is poor due to the difficulty in attaining equilibrium in a system which is predominantly solid.

The free energy change of the reaction

$$2 NdCl_{3(l)} + Nd_{(s)} = 3 NdCl_{2(l)}$$
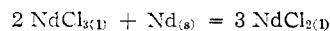
calculated from the composition of the presumed ideal liquid in equilibrium at the peritectic temperature of 841° is −11 kcal. The value of −165 kcal. mole^{-1} obtained with the acid of estimated free energy functions[24] for $\Delta H_{298}°$ for the formation of $NdCl_2$ compares well with −175 ± 10 kcal. mole^{-1} estimated by Brewer, *et al.*[24]

The Nd–NdI₃ System.—The most striking feature of this system, shown in Fig. 3, is the reduction of neodymium to an apparent oxidation state below two. As contrasted to the neodymium chloride system, where three lower halides are formed, only one lower iodide is found. Both cooling curve data and equilibrations above and below the melting point of this iodide indicate a compound of the composition $NdI_{1.95}$ ± 0.01, melting congruently at 562°. The salt is a shiny black color in bulk and a dark red-violet when finely ground.

The melting point found for the light green NdI_3 is 787°, with a phase transformation at 574°,

(575°[28]). The eutectic is at 26.6% Nd and 491° and the limit of the reduced phase, 35.0% at 562°. During early runs metal added to the salt containing 28 to 33% metal often remained on the surface of the salt, perhaps because of high surface tension, and so failed to react completely. Because of this, it was originally assumed that $NdI_{2.0}$ was the product. However, mixtures of NdI_3 and metal, made up to $NdI_{2.00}$ and carefully equilibrated, still exhibited a eutectic halt, and the X-ray powder patterns showed faint traces of NdI_3. Numerous, subsequent phase studies established the indicated iodide deficiency. Two experiments on $Sm-SmI_2$ at 650°, 130° above the melting point of the diiodide,[28] showed the limiting composition of the liquid to be $SmI_{1.91} \pm 0.02$.

Structurally, the neodymium and samarium "diiodides" are quite dissimilar; however, $NdI_{1.95}$ is isostructural with $SrBr_2$ (and $SmBr_2$ and $EuBr_2$[26]). Because of the uncertainty regarding the interpretation of the $SrBr_2$ structure,[29] no attempt was made to index the powder pattern.[30] The apparent reduction of neodymium, and perhaps also samarium, below the dipositive state is both surprising and in contrast to the behavior of the chloride. At present it is not possible to distinguish between two obvious possibilities, the presence of "free" electrons or the formation of Nd^+, although the insulating character of the solid appears to mitigate against the former. Further investigation of this point is in progress.

The (Ce, Nd)-($CeCl_3$, $NdCl_3$) System.—As already mentioned, some controversy has arisen concerning the experimental conditions of physical studies on $Ce-CeCl_3$ melts and the interpretation of the data as 'proof' of the formation of the unique ion Ce^{+1}[2–14] On the other hand, if the more conventional Ce^{+2} were to be formed when cerium dissolves in its molten trichloride, it should be possible to substitute this for Nd^{+2} in a reduced neodymium phase since Ce^{+2} is probably only about 0.04 Å. larger than Nd^{+2}. A series of equilibrations were therefore carried out with various Nd/Ce ratios in the melt and with excess neodymium metal, the cerium being added as the metal and/or the trichloride. As would be expected, the over-all limit of reduction when neodymium and cerium are present in comparable amounts is less than when a large excess of neodymium is present.

Evidence suggestive of the incorporation of Ce^{+2} in the phase $NdCl_{2.37}$ is furnished by the composition and powder patterns of the solids obtained from melts in which the Nd/Ce ratio was between one and two. For samples in which the final Cl/M was equal to 2.38, 2.34 and 2.28, with corresponding Nd/Ce ratios of 1.22, 1.52 and 1.72, respectively, the per cent reduction of cerium to the assumed Ce(II) calculates to be 16, 15 and 24%, respectively, if all the neodymium is assumed to be present only as Nd(II), the most unfavorable cir-

(28) A. H. Daane and D. H. Dennison, private communication.

(29) A. F. Wells, "Structural Inorganic Chemistry," Oxford Univ. Press, London, 1950, p. 272.

(30) The strongest lines of $SrBr_2$ cannot be indexed with the lattice constants reported by Kamermans (Z. Krist., 101, 406 (1939)) but can be if c_0 is doubled.
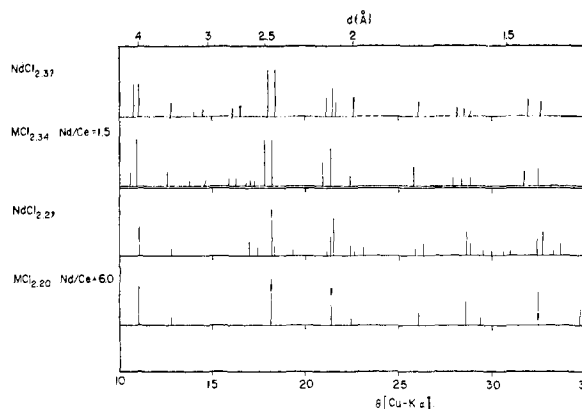
Fig. 4.—Comparison of powder patterns for the intermediate neodymium chlorides with those of the mixed neodymium-cerium chlorides.

cumstance possible. There was definitely no evidence for the contamination of these samples by free metal. For products with higher Nd/Ce, and therefore lower Cl/M ratios, the stoichiometry alone allows the cerium to be entirely trivalent.

Although no attempt was made to establish the composition of the pure phase(s) in these mixed samples, the above $MCl_{2.34}$ sample is evidently close to this point, as it structurally essentially identical with $NdCl_{2.37}$, as shown in Fig. 4. Although the structure of the latter phase is unknown, it logically can be considered to contain both Nd^{+2} and Nd^{+3}, so that the mixed product apparently can be regarded to result from substitution of Ce^{+2} in some of the divalent Nd^{+2} positions as well as Ce^{+3} in most if not all of the trivalent sites.

An interesting structure transformation is also found in this mixed system with higher Nd/Ce ratios in that the presence of cerium in the solid, presumably as Ce^{+3}, results in the formation of the simple, face-centered-cubic structure ($a_0 = 7.04$ Å.). With Cl/M equal to 2.19 and 2.20 and Nd/Ce of 6.05 and 4.51, respectively, the powder patterns contain no lines that cannot be accounted for by this fluorite structure (Fig. 4).

That trivalent chlorides can be incorporated into the fluorite lattice of divalent chlorides has been recently shown by Brauer and Müller,[31] who were able to dissolve up to 22.5% $LaCl_3$ into $SrCl_2$ without disrupting the latter's fluorite structure. From density and lattice dimension measurements, they concluded that the La^{+3} ion occupies a normal cation site in the $SrCl_2$ lattice with the extra chloride positioned in the body center of the unit cell. Since there are four dihalides per unit cell, it should be theoretically possible to add up to 25% trichloride to a dichloride in such a structure to form $MCl_{2.25}$ ($MCl_3 \cdot 3MCl_2$ or M_4Cl_9). By analogy with $LaCl_3$ in $SrCl_2$, the net effect of the addition of chloride ions to the body center, together with the concomitant substitution of Ce^{+3} for Nd^{+2}, would be to expand the unit cell over that for Nd-

(31) G. Brauer and O. Müller, Z. anorg. allgem. Chem., 295, 218 (1958), Other examples of this type of substitution are found with $(Ce_{0.55}U_{0.45})O_{2.3}$ (W. Rüdorff and G. Valet, ibid., 271, 257 (1953)) and in the systems CaF_2-YF_3 and SrF_2-LaF_3 (E. Zintl and A. Ungard, ibid., 240, 150 (1939)).

Cl_2 in the fluorite structure. On the other hand, if the anion lattice were to remain intact, the result of substitution of 2 Ce^{+3} and a cation vacancy for 3 Nd^{+2} would result in a smaller unit volume. Several different estimates of the radius of Nd^{+2} from those of Eu^{+2}, Yb^{+2} [26] and Pb^{+2} and the size of the stable $NdCl_2$ structure are all in the range of 1.16 to 1.21 Å. Since the corresponding cell volume of 323 to 339 Å.[3] for $NdCl_2$ in the CaF_2 structure compares to 349 Å.[3] observed for (Nd, Ce)$Cl_{2.20}$, substitution of the type suggested by Brauer and Müller seems probable for this mixed phase. Judging from Fig. 4, it may be that Nd-$Cl_{2.27}$ has a related, distorted fluorite structure, since there is a close correspondence between the strongest lines in this pattern and those of $MCl_{2.20}$. Such a rhombohedral unit cell has been suggested for $YbCl_2$.[26]

Experimental

Preparation of the Rare Earth Metal Trihalides.—Common procedures for the preparation of the anhydrous halides start with the oxide,[32,33] the hydrated halide[34,35] or an easily decomposed salt such as the acetate[36] or the benzoate,[32,37] and heat these in the presence of a suitable halogenating agent, such as NH_4X or HX. Since in all of these methods, the problem of oxyhalide contamination is likely to be serious, especially with the iodides, a procedure was therefore devised which would minimize such contamination.

As the metals are now available in a high state of purity, the use of these as starting materials in the preparation of the halides by direct reaction with either the halogen or the hydrogen halide is advantageous. However, at temperatures above the melting points of the halides (700–900°) the metals react vigorously with virtually all non-metals and their compounds, forming compounds which usually are more stable than the desired halide. Although a metallic container is therefore desirable, most metals suitable for containers are themselves subject to attack under these conditions, or in the case of the noble metals, react with the lanthanides to form very stable intermetallic compounds. However, thermodynamic calculations by Brewer, et al.,[38] indicate that under proper conditions, molybdenum and tungsten should serve as suitable container materials for the preparation, having the advantage that they react with neither the lanthanides nor their halides. Although either material is readily attacked by chlorine, their reaction with HCl is a function of the partial pressure of hydrogen, and this can be easily regulated. Thus, Brewer estimates that to maintain a gaseous halide pressure of less than 10^{-5} atm. at 800°, log (P_{HCl}/P_{H_2}) should be less than 4 for molybdenum and 6 for tungsten. Because of its relative ease of fabrication, molybdenum was chosen as the container material. Similar data show that a tungsten container can be used in the preparation of the iodides with a total iodine pressure of at least 0.1 atm. at 800°, 1 atm. at 600°, before the WI_2 pressure exceeds 10^{-5} atm., while for molybdenum, the allowable iodine pressure is only 10^{-3} atm. under the same conditions.

Due to the extreme hydroscopic nature of all of these salts and the reactive nature of the metals and the subsequently-prepared subhalides, all of these were stored in evacuated sample containers or sealed ampoules, and all transfers were carried out in an argon-filled glove box.

Chlorides.—Neodymium and cerium trichlorides were prepared by the reaction of the metal with anhydrous hy-

drogen chloride at a temperature above the melting point of the trichloride. The reaction was carried out in a fused silica tube connected to a gas purification train. About 11 grams of metal turnings (Ames Lab., 99.9%; metallic impurities: <0.1%, principally Ca, Mg, Ta; non-metallic: < 300 p.p.m. N, F, C, < 600 p.p.m. O) were placed in a molybdenum boat, 4″ × 3/4″ × 3/4″, and this in turn was surrounded by a molybdenum cylinder to prevent attack of the silica by any metal that might splatter in the course of the reaction. The incoming gases (hydrogen, hydrogen chloride, helium) were dried by passing them through a sulfuric acid bubbler and a −80° trap. The outlet tube was fitted with a stopcock and a sulfuric acid bubbler. Since the hydrocarbons found in commercial HCl are difficult to remove and react preferentially with the lanthanides, the HCl was generated as required by dropping concd. H_2SO_4 on dry KCl.

Before each run, the apparatus and contents were thoroughly flushed with helium, and a slight helium flow was maintained while the reaction tube was heated to temperature. When the HCl flow was initiated, the hydrogen generated by the reaction was sufficient to prevent attack of the molybdenum. With a moderately fast flow rate, thirty to fifty minutes were usually sufficient for complete reaction, and this was signaled by the appearance of white fumes of molybdenum chloride in the outlet tube. At this point, the HCl flow was decreased, the hydrogen flow increased until it was about one half that of HCl and the apparatus maintained at temperature for another fifteen to thirty minutes. During the cooling, helium was circulated through the apparatus. The salt obtained by this procedure was in a massive crystalline form and was easily removed from the molybdenum boat. Spectroscopic analysis of the final salt revealed only trace metallic impurities known to be in the original metal. Any molybdenum present was below the limits of detection by spectroscopic means (< 0.1%) or by spot tests. Three analyses of one preparation by a vacuum distillation and fusion method[39] gave an oxygen content of 570 ± 40 p.p.m.; this includes that picked up during handling in the dry box and in a rapid transfer in air into the vacuum fusion apparatus. A similar procedure should also be suitable for preparation of the bromides.

Iodides.—Neodymium triiodide was prepared by the reaction of the metal with iodine in an evacuated, fused silica apparatus at 800°. About 12 grams of metal turnings were placed in a tungsten crucible, 1¼″ o.d. × 1″ i.d. × 2″, (Kulite Tungsten Corp., Ridgefield Park, N. J.) while the iodine (B & A Reagent Grade), previously purified by vacuum sublimation at 80°, was contained in a sidearm. The entire apparatus was evacuated and sealed off and the section of the apparatus containing the metal was then heated to 800° while the sidearm containing the iodine was heated to 185°. Three hr. were allowed for complete reaction. The crucible was maintained at 250–300° for several hours while the iodine sidearm was immersed in a −80° trap to condense out any unreacted iodine, and the latter was then sealed off. Spectroscopic analysis of the asbestos-like product revealed only trace impurities known to have been in the metal; tungsten present was below the limits of detection (<0.1%).

Phase Studies.—Equilibrations of the salts with metal were carried out in a 29 mm. × 18″ fused silica tube fitted with a standard taper joint which joined to a Pyrex top fitted with a stopcock and ball joint to allow for evacuation. The metal and salt were contained in a crucible, 1″ × 5/8″ i.d., fabricated from 5 mil. tantalum. Best results were obtained if the metal turnings were first melted into a button before equilibration with the salt; otherwise these disintegrated during the reaction, and the fine metal chips were difficult to separate from the salt phase afterwards. Before heating, the apparatus was evacuated with a mercury diffusion pump and one-half atmosphere of dry argon then admitted to the tube. An equilibration time of one or two hr. was usually sufficient for liquid salts, while two to five hr. was found to be adequate with a solid phase. Quenching of the sample was accomplished by plunging the hot tube into cold water, after which the metal could easily be separated from the salt.

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Because of the high temperatures, thermal analysis was employed for the remainder of the phase diagram. For this, a three section apparatus was constructed so that successive additions of metal could be made in the course of the study. The bottom section was constructed of 29 mm. × 14″ fused silica with a vacuum jacket of 41 mm. fused silica on the lower two thirds. A platinum foil radiation shield was placed around the outside of the vacuum jacket. The middle segment of the apparatus consisted of a Pyrex "el," while the top, also of Pyrex, had a stopcock and two tungsten-through-glass seals for the thermocouple leads. The "el" was necessary to avoid thermal gradients across the tungsten leads. A small blower was used to cool the connecting taper joints and the stopcock. The sample itself was contained in a tantalum crucible, $^3/_4''$ i.d. × 2″, with a thermocouple well of $^5/_{32}''$ tantalum tubing positioned in the center and crimped so that the tip of the thermocouple was $^1/_4$ to $^1/_2''$ above the bottom of the crucible. The #28 gauge chromel-alumel thermocouple was encased in an alundum shield and was equipped with small alligator clips to facilitate easy replacement.

The vacuum-jacketed portion of the apparatus was positioned in a resistance furnace, the ends of which were well packed with Fiberfrax insulation (Carborundum Co.). With power off, this apparatus had a maximum cooling rate of 7°/min. at 800°. The thermocouple potentials were recorded by a potentiometer equipped with a variable, 2–10 millivolt scale and a 0–40 millivolt zero suppression, and a Rubicon potentiometer was subsequently used to measure the recorded thermal arrests. The thermocouple in the apparatus was standardized regularly against NaCl, NaI and KCl, using the recently reported melting points[3,4]; the couple was replaced if the experimental results varied from those reported by more than one degree. No provision was made for agitating the sample during cooling other than by shaking the entire apparatus by hand.

The procedure followed in a run was to load a sample of about 25–35 millimoles of salt in the dry box and evacuate to 10^{-6} mm. for about 1 hr. One-half atmosphere of dry argon was then introduced so as to keep sublimation of the trihalides to a minimum, and the sample equilibrated at the desired temperature for at least 1 hr. before a cooling curve was run. Thermal halts were reproducible to within 1° on a given sample, and unless otherwise noted, all temperatures reported are ±1°. The entire apparatus was returned to the dry box for addition of further metal. In spite of vigorous shaking of the apparatus, supercooling was particularly bad for the neodymium iodide system at $NdI_{1.95}$.

Samples for analysis were transferred in the dry box to a weighing bottle and weighed in air. After transfer of the sample, the bottle was again weighed and the necessary bouyancy correction applied. The salts were contacted with water and, after any initial reaction had subsided, sufficient 1.5 N H_2SO_4 was added to dissolve any hydrolysis products. An acid solution was not added directly to the

subhalides as the reaction was violent enough to ignite the evolved hydrogen. With the iodides, a small amount of sodium sulfite was added to prevent air oxidation to iodine.

Where only one cation was present or where total lanthanide content was desired, the metal was titrated with EDTA using arsenazo indicator at pH 7.[40] Where mixed salts of two lanthanides were involved, the individual lanthanides were determined spectrophotometrically by the Analytical Service Group by the method of Banks and Klingman.[41] Chloride was determined gravimetrically while iodide was titrated with silver nitrate using Eosin Y as the indicator. The analyses were considered reliable if the material balance totaled 100 ± 0.3 wt. %. In the results quoted, unless otherwise noted, the values of mole per cent metal are ±0.3% and halide to metal ratios are ±0.01.

Powder Pattern Determination.—Samples for X-ray powder patterns were loaded in the dry box into 0.1–0.3 mm. i.d. Pyrex capillaries and sealed off. Diffraction patterns were obtained using Ni-filtered, Cu-Kα radiation in an 11.46 cm. Debye–Scherrer camera. Values for the metals, $NdCl_3$ and NdOCl, obtained agreed very well with those reported in the ASTM file[42] and so are not included. Only in samples where contamination had been known to occur were a few of the stronger oxyhalide lines observed weakly; no sign of oxygen contamination was evident in regular samples.

The stronger lines and intensities for $NdCl_{2.37}$, $NdCl_{2.27}$, $NdCl_2$, NdI_3 and $NdI_{1.95}$ are:

$NdCl_{2.37}$: 4.11(7), 4.00(7), 3.48(4), 2.78(2), 2.71(2), 2.50 (10), 2.44(10), 2.14(4), 2.11(6), 2.09(3), 2.01(3), 1.75(3), 1.46(4), 1.43(3).

$NdCl_{2.27}$: 4.01(6), 2.64(3), 2.47(10), 2.12(4), 2.10(7), 2.02(2), 1.74(3), 1.61(5), 1.60(3), 1.435(4), 1.425(5), 1.343(3).

$NdCl_2$: 4.03(7), 3.88(7), 3.79(5), 3.57(7), 2.77(10), 2.51(6), 2.47(6), 2.38(5), 2.27(7), 2.15(5), 2.10(6), 1.96(4), 1.945(4), 1.605(3), 1.585(4).

NdI_3: 6.86(8), 3.48(4), 3.28(4), 3.15(6), 2.99(10), 2.85(6), 2.57(6), 2.28(6), 2.11(8), 1.909(5), 1.808(5), 1.745(5), 1.719(5), 1.703(5), 1.686(5), 1.660(5), 1.517(6), 1.505(6), 1.337(7), 1.312(6).

$NdI_{1.95}$: 4.52(3), 3.65(3), 3.51(7), 3.26(3), 3.16(8), 2.82-(10), 2.81(7), 2.75(6), 2.32(3), 2.15(2), 1.986(3), 1.776(4), 1.745(3), 1.607(4), 1.513(4), 1.481(3), 1.434(3).

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Coördination Compounds Derived from Polymeric Schiff's Bases[1]

By Harold A. Goodwin[2] and John C. Bailar, Jr.

Triethylenetetramine has been condensed with 5,5'-methylene-bis-salicylaldehyde and bis-salicylaldehyde-5,5'-sulfone to obtain polymeric Schiff's bases containing recurring sexadentate units. The thermal stabilities of complexes derived from these polymers and a series of bi- and trivalent metal ions have been examined. Condensation of the above aldehydes with diethylenetriamine or 2,6-bis-(aminomethyl)-pyridine gave polymers containing five donor atoms per unit. Complexes derived from these and trivalent metal ions were prepared and were shown to exhibit greater thermal stability than the corresponding complexes derived from the sexadentate polymers.

Schiff's bases (Ia and Ib) derived from o-phenylenediamine and the dialdehydes, bis-salicylalde-

hyde-5,5'-sulfone and 5,5'-methylene-bis-salicylaldehyde, have been shown[3,4] to coördinate with bivalent metal ions yielding neutral coördination polymers.

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