(III) salts are distorted, presumably along one axis giving rise to D_{4h} symmetry. We feel the extent of distortion parallels the extent of splitting of the Co–N stretching mode. This indicates that the sodium salt is most distorted, followed by the barium salt, and then the $[Co(en)_3]^{3+}$ salt.

The electronic spectra of the cesium, sodium, and barium salts justify the conclusion that compounds exhibiting a split Co–N stretching mode are distorted. Wentworth and Piper[3] have developed a three-parameter crystal-field model for cobalt(III) (and chromium(III)) complexes. Table II contains the observed electronic spectral data for hexanitrocobalt(III) salts and our assignments. The assignments for the cesium salt are self-consistent; using our assignments for the energies of the $^3T_{1g}$, $^3T_{2g}$, and $^1T_{1g}$ energy levels we calculate the energy of the $^1T_{2g}$ level. A calculated value of 25,300 cm^{-1} agrees very well with that observed (25,200). No other choice of assignments is so self-consistent, and we feel these to be correct.

Using Wentworth and Piper's model, we assume that the cesium salt possesses undistorted octahedral cobalt(III) on the basis of the cesium bromide region spectrum and calculate the Racah parameters B and C; values of 56.2 cm^{-1} for B and 4550 cm^{-1} for C are obtained. This value of B is considerably below those observed for a number of other compounds. Wentworth and Piper[3] calculate values of 528, 502, and 418 cm^{-1} for the hexaammine-, tris(ethylenediamine)-, and hexacyanocobalt(III) complexes. However, low values of B in cobalt(III) complexes are not unknown. From data given by Jørgensen[4] we calculate a B value of 22 cm^{-1} for the diethyldithiophosphate complex of cobalt(III). Using our value of B for $Cs_3[Co(NO_2)_6]$, we calculate the nephelauxetic parameter $1 - \beta$ and obtain a value of 0.95. From this we conclude that the hexanitrocobalt(III) complex exhibits a very high degree of covalency.

For the cesium salt we calculate a Dq of 2880 cm^{-1}. Considering that the nitrite ion lies between ethylenediamine and cyanide ion in the spectrochemical series, this appears to be a logical value; Dq values for the cobalt(III) complexes of these two ligands have been calculated to be 2530 cm^{-1} (ethylenediamine) and 3600 cm^{-1} (cyanide ion).[3] However, our calculated value is somewhat lower than those determined by Wentworth and Piper (ranging between 3120 and 3262 cm^{-1}).[3]

The distorted anions (present in the barium and sodium salts) are assumed to have D_{4h} symmetry; the equatorial nitrites are assigned the same value of Dq that they have in the O_h complex.[3] Calculating Dq' for the axial ligands we obtain values of 1860 cm^{-1} for the sodium salt and 2280 cm^{-1} for the barium salt.

Two explanations may be advanced to explain these data. The lowered Dq' values could be accounted for by the oxygen end of the NO_2^- ions interacting with the cations in the crystal lattice. This would result in the electron density being shifted away from the central cobalt(III), thereby reducing Dq'. However, unless all six nitrites are affected in this fashion (which would maintain O_h symmetry), one would expect a much more complicated spectrum than observed. In addition to Co–N modes, new vibrations for the nitrites of lowered symmetry should be present.

These spectra are much more compatible with a different interpretation. A splitting in the Co–N stretching mode indicates a distortion, probably induced by the crystal lattice, from O_h symmetry. The calculated Dq' values for the axial ligands show that this distortion is one of elongation along the z axis; compression should, of course, be indicated by higher Dq' values.

Electronic and vibrational spectra very nicely complement each other in this series of compounds. In the infrared spectrum the extent of splitting of the Co–N mode correlates qualitatively with the shift of the Dq' values from Dq; both probably correlate with the degree of distortion from O_h symmetry.

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Rare Earth Metal–Metal Halide Systems. IX. The Dysprosium–Dysprosium(III) Chloride System and the Preparation of Dysprosium(II) Chloride[1]

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Phase studies of many metal–metal halide systems for the lighter rare earth metals have revealed that solid, intermediate phases exist in a number of instances and that, in general, the stability of the dipositive states increases rather regularly from lanthanum to europium.[2–4] Similar studies of the heavy rare earth metal systems have been less extensive. The existence of ytterbium(II) salts has been long known, while a stable dipositive state for thulium, the preceding element, has been predicted by Brewer, *et al.*,[5] and more recently by Polyachenok and Novikov[6] for the chloride and actually

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[1] Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Contribution No. 1830.

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[3] L. F. Druding and J. D. Corbett, *J. Am. Chem. Soc.*, **83**, 2462 (1961).

[4] J. E. Mee and J. D. Corbett, *Inorg. Chem.*, **4**, 88 (1965).

[5] L. Brewer, L. A. Bromley, P. W. Gilles, and N. L. Lofgren in "Chemistry and Metallurgy of Miscellaneous Materials: Thermodynamics," L. L. Quill, Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1950, p 123.

[6] O. G. Polyachenok and G. I. Novikov, *Russ. J. Inorg. Chem.*, **8**, 816 (1963).

realized by Asprey and Kruse[7] as the iodide. Although Polyachenok and Novikov also predicted that erbium, the next lighter element, should form the stable $ErCl_2$, recent work reveals that no intermediate solid phases are formed in either the Er–$ErCl_3$ or the Er–ErI_3 systems.[8] The only other phase studies of the heavy group halides have been for gadolinium, where the solids $GdCl_{1.6}$ and GdI_2 have been found to be stable with respect to disproportionation.

Although the intervening element dysprosium might by analogy be considered an unlikely candidate for formation of stable, reduced halide phases, Dworkin and co-workers[9] in the course of a conductivity study found the metal reaction limit in $DyCl_3$ to be about 28 mole % Dy at 700°. Such an extensive reaction suggests that a solid subchloride may be formed, and the present study of the phase diagram reveals that two intermediate compounds are present.

Experimental Section

Materials.—Dysprosium metal used for reduction of $DyCl_3$ was available in the Ames Laboratory in high purity. Typical impurity analyses showed 360 ppm O, 20 ppm N, and <0.1% metallic impurities, principally as Ta, Ca, Fe, and other rare earth metals, the most common of which was Tb. $DyCl_3$ was prepared as before,[3] except that commercial HCl was used, and the product was then twice distilled under high vacuum at 800 to 875°. Analyses[10] of the sublimed salt gave Cl/Dy = 2.99 ± 0.02 and material balances of 100.0 ± 0.3%.

Phase Studies.—Thermal analysis data were obtained as recently described.[8] Each sample was sealed in a tantalum crucible, 0.50-in. i.d. × 2-in. height, equipped with two lengths of 0.156-in. diameter tubing welded through the lid and closed at the inner and outer ends, to serve as a thermocouple well and an addition port, respectively. Subsequent additions of metal were made through the latter by cutting off the sealed tip in a drybox and then afterward crimping the tip of the addition port such that it could be rewelded. Final analyses agreed with the material added within 0.2 mole %, with Dy + Cl recovery of 100.0 ± 0.3%.

The apparatus for equilibration studies has also been described.[4] For these, excess metal as a lump was placed into the closed end of a 0.25-in. diameter tantalum tube, and $DyCl_3$ was added in a drybox. The open end of the sample tube was sealed by welding, and the sample was heated briefly to 700° in order to reduce the volume of the salt through fusion. Subsequently, the tube above the sample was flattened to prevent volatilization. Good reproducibility of the saturation limit was obtained with 7- to 18-hr equilibration at temperature.

To secure samples for powder patterns at various metal–chloride compositions, mixtures of the desired stoichiometry were equilibrated in tantalum for a few hours at a temperature above the melting point of any solid phase, quenched to avoid phase segregation, and then equilibrated at 625° for at least 3 days.

Results and Discussion

The salt-rich portion of the $DyCl_3$–Dy system is shown in Figure 1. The metal solubility is seen to be quite substantial, 15 mole % at the 507° eutectic and 31.0 mole % at 800°. There are two intermediate phases present—$DyCl_{2.1}$ (29.6% Dy), decomposing incongruently at 675° into $DyCl_2$(s) and liquid of composition about $DyCl_{2.15}$, and $DyCl_2$, which at 721° is in equilibrium with Dy(s) and a liquid about $DyCl_{2.08}$. It now appears that the reported limiting reaction of ~28% Dy at 700°[9] represents the composition of the liquid phase in equilibrium with solid $DyCl_2$; the present phase diagram yields a comparable value of 29% at this temperature.

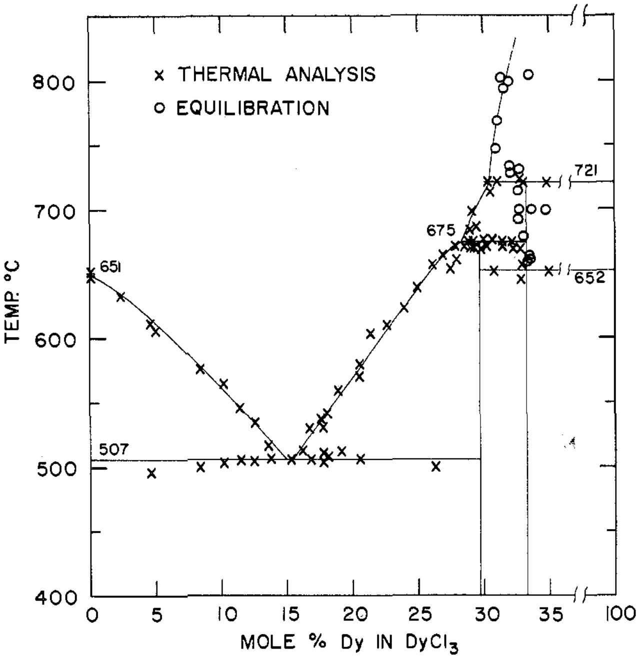

Figure 1.—Phase diagram of the dysprosium(III) chloride–dysprosium system.

A few points regarding this description of the phase relationships require comment. First, three equilibration points at ~730° are seen to the right of the liquidus curve. These points are believed to be in error since location of the liquidus curve below the 721° peritectic as well as observations of this halt itself dictates the construction shown in this region. Further, should the lower liquidus curve intercept the peritectic line at 32.8 mole % metal as might be indicated if the points in question were correct, this would result in a sizable retrograde effect which is rare in such diagrams and is unknown among rare earth systems. Possible explanations for the apparent error in these points are thermal gradients in the furnace, poor contact of the internal measuring thermocouple with the sample container, so that the actual temperature was below the apparent 721° peritectic temperature, or a low value for this melting point itself. Considerable care was taken to avoid the first two possibilities, and no indication of supercooling was observed; nonetheless, the points probably pertain to the composition of the solid $DyCl_2$ rather than the liquidus at a slightly higher temperature.

The 675° peritectic decomposition exhibited substantial supercooling, 5 to 10° even on slow cooling, which accounts for the scatter of points in this region. When cooling curves were run from ~750° on samples containing excess metal, the supercooled peritectic was evidently responsible for an arrest observed at 646°

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[8] J. D. Corbett, D. L. Pollard, and J. E. Mee, *Inorg. Chem.*, **5**, 761 (1966).

[9] A. S. Dworkin, H. R. Bronstein, and M. A. Bredig, *J. Phys. Chem.*, **67**, 2715 (1963).

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since the effect was absent with such samples equilibrated below 721° and then cooled or with samples not containing excess metal. The additional 652° point was properly detected over a range of compositions and appears to be the result of a phase transformation in $DyCl_2$. The high-temperature form could not be quenched to room temperature.

The freezing point depression of $DyCl_3$ for dilute solutions of metal is quite consistent with the presence of an oxidation–reduction reaction on metal "solution" which produces monomeric Dy^{2+} ions. In fact, the solutions appear nearly ideal, and the entropy of fusion of $DyCl_3$ which would make the data up to even 10 mole % Dy (30% Dy^{2+}) consistent with this model is close (6.4–6.7 eu) to the 6.8 eu extrapolated from known values for the neighboring $HoCl_3$ and $ErCl_3$.[11]

The two stable lower chloride phases are both black, electrically insulating, and highly susceptible to attack by air. The stoichiometry $DyCl_{2.11\pm0.02}$ for the higher one was estimated on the basis of X-ray powder patterns of equilibrated mixtures plus the liquidus composition at its melting point as an upper limit. Patterns at $DyCl_{2.12}$ and $DyCl_{2.09}$ were those of this phase, $DyCl_{2.06}$, a mixture, and $DyCl_{2.02}$, that of $DyCl_2$. The two phases give somewhat similar patterns and are presumably related by a $3Dy^{2+} = 2Dy^{3+}$ substitution. The low-temperature form of $DyCl_2$ is isostructural with $YbCl_2$ as reported by Döll and Klemm,[12] with lattice constants derived for the same orthorhombic symmetry of a_0 = 6.69 A, b_0 = 6.76 A, c_0 = 7.06 A, 0.08 to 0.15 A larger than given for $YbCl_2$.

The saltlike character of $DyCl_2$, its relationship to the known $YbCl_2$, and the cryoscopic evidence given above leave little doubt that the compound is properly considered as a simple dysprosium(II) salt. It is unfortunate that magnetic data cannot be expected to confirm the presence of Dy^{2+} because of the near coincidence of the theoretical moments for Dy^{3+} and Dy^{2+} (Ho^{3+}), 10.63 and 10.60 BM, respectively.[13]

The relatively substantial reduction demonstrated for dysprosium(III) is followed by a lesser amount reported for holmium (18.5% or $HoCl_{2.44}$),[9] a more limited reaction of Er with $ErCl_3$ (5%),[8] and then by a greatly enhanced stability of thulium(II) (at least as TmI_2[7]) and ytterbium(II). Consequently, there is little resemblance of reduction tendencies of the heavy half of the lanthanides to the simple regularity found in the first half. Nonetheless, it appears that the extent of reduction of all of these elements can be rather simply interpreted in terms of the prime importance of the enthalpy of sublimation of the metals themselves, with small variation in the known ionization energies being of secondary importance.[8] Thus, in the present case it is the relatively low $\Delta H^\circ_{\text{sub}}$ of dysprosium metal which appears principally responsible for the relatively ready reduction.

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Proton Magnetic Resonance Spectra of Aquated Bis(ethylenediamine)cobalt(III) Ions

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Although the bis(ethylenediamine)cobalt(III) complex ions have been of considerable interest in the study of reaction mechanisms and bonding of octahedral complexes, they have been examined only briefly with nuclear magnetic resonance techniques.[1-3]

The amino proton peaks of bis(ethylenediamine)cobalt(III) complexes appear in the same spectral range as the water peak and hence are difficult to observe. Clifton and Pratt[1] used deuterium oxide as solvent and noted the gradual disappearance of the amino peaks as the attached protons are replaced by deuterium. Recently Jolly, Harris, and Briggs[4] reported nmr examination of some of the ammine complexes of cobalt(III) in concentrated sulfuric acid. This was attempted with bis(ethylenediamine) complexes, but it was found that rapid oxidation of the ligands ensued. However, it was discovered that a given amino peak could be made visible by a judicious increase of the acidity to shift the water peak downfield; solutions up to 8 *M* in sulfuric acid were successfully used although it was found that use of perchloric acid resulted in better resolution. Deuterium oxide was also employed when desirable although again the HDO peak tended to obscure one or more of the amino proton peaks in acidic solution. In neutral or basic solutions, the amino peaks disappear completely because of rapid exchange of the amino and water protons.[5]

The nmr spectrum of the highly symmetrical *trans*-diaquobis(ethylenediamine)cobalt(III) ion in acidic solution consists of two broad singlets at 1.88 and 4.58 ppm downfield from *t*-butyl alcohol used as an internal standard, with the former assigned to the eight methylene and the latter to the eight amino protons (Figure 1A). The observed broadening of the amino peaks is anticipated because of nuclear quadrupole relaxation effects[6] while broadening of the methylene proton peaks is due to a slight degree of coupling with the amino protons. The broadening is gradually eliminated in deuterium oxide solution, and the amino peak disappears as the amino protons are replaced by deuterium.

The position of the methylene proton peak is pH-dependent, varying from 1.88 ppm at pH 4 or below to 1.58 ppm at pH 9 or above. The change in the chemical shift corresponds to the ionization of the diaquobis-

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