

NO_2^- (also for py with the data available), and furthermore since ionic strength effects usually are negligible in all platinum(II) reactions, the totally first-order rate interpretation seems reasonable.

It is interesting to compare the second-order rate constants for Cl^- and NO_2^- , obtained from

TABLE III
BIMOLECULAR RATE CONSTANTS IN WATER SOLUTION AT 25° FOR Cl^- AND NO_2^- AS REACTANTS FOR SEVERAL PLATINUM(II) COMPLEXES^a

| Complex | $k_2 \cdot 10^4 \text{ M}^{-1} \text{ sec.}^{-1}$ | |
|--|---|--------------------|
| | Cl^- | NO_2^- |
| $\text{Pt}(\text{dien})\text{H}_2\text{O}^{2+}$ | 1×10^4 | 0.56×10^4 |
| $\text{Pt}(\text{dien})\text{Br}^+$ | 8.8 | 37 |
| $\text{Pt}(\text{NH}_3)_3\text{Cl}^+$ | 0.7 | 87 |
| <i>trans</i> - $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ | 7.8 | $>10^4$ |
| PtCl_4^{2-} | ~ 0 | $>10^4$ |

^a Data not reported in this work taken from ref. 10.

the slopes of the lines shown in Fig. 1. Nitrite ion actually reacts slower than chloride with this doubly charged platinum(II) complex cation, in sharp contrast to the relative reactivities of these ions with neutral and negatively charged platinum(II) complexes. These data are given in Table III. There is a dramatic decrease in the NO_2^- to Cl^- reactivity ratio in going from PtCl_4^{2-} to $\text{Pt}(\text{dien})\text{H}_2\text{O}^{2+}$, which is consistent with the proposal that the NO_2^- attack on platinum(II) is mainly electrophilic, while the Cl^- attack is mainly nucleophilic.¹⁰

Acknowledgments.—The authors are indebted to Professor Ralph G. Pearson for several suggestions during the course of this work. This work was supported by the National Science Foundation.

CONTRIBUTION FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY,
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The Solid Rare Earth Chelates of Ethylenediaminetetraacetic Acid¹

By R. S. KOLAT AND J. E. POWELL

Received June 23, 1961

The solid acidic chelates formed by the reaction of the tripositive rare earth ions with the protonated ethylene, diamine-N,N,N',N'-tetraacetate ligand have been studied by means of thermobalance, infrared, and X-ray diffraction measurements. The oven-dried (110° for 24 hr.) chelates of cerium through samarium were found to be monohydrated, while the remaining members were anhydrous. Infrared studies suggested that the change in hydration number was accompanied by a change in the amino acid ligand from a pentadentate to a hexadentate configuration. Measurements of the acid dissociation constants of these chelates indicated that a corresponding change does not take place in solution.

Introduction

The ability of ethylenediaminetetraacetic acid (abbreviated $\text{H}_4(\text{EDTA})$) to form exceptionally stable chelates with the trivalent rare earth ions (abbreviated Ln) is well known. The study of these chelates was initially of a practical nature since differences in the stability constants of chelates of adjacent rare earth ions afford a means of separating rare earth mixtures in ion-exchange systems.² However, since the rare earths constitute a series of trivalent ions with

gradually decreasing radii, they offer an excellent opportunity to study the theoretical aspects of chelation. Conversely, the study of chelation has afforded a means of comparing the individual properties of rare earth ions. It has been shown that the stabilities of rare earth chelates generally increase as the atomic number increases due to the so-called lanthanide contraction.

Most of the published information on the rare earth chelates has been concerned with their properties in aqueous solutions. Studies of the solid compounds have been limited to several preliminary investigations of rare earth-EDTA chelates. Brintzinger and his co-workers have reported the preparation of the compounds

(1) Contribution No. 1030. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

(2) F. H. Spedding and J. E. Powell, *Chem. Eng. Progr., Symp. Ser.*, **50**, No. 14 (1954).

H[La(EDTA)], H[Nd(EDTA)], and Y[Y(EDTa)]₃.³ Moeller and his associates have reported on the nature of the solid acid chelates H[Ln(EDTA)] and their sodium salts.⁴ They examined several of the lighter rare earth chelates using infrared spectroscopy, differential thermal analysis, X-ray diffraction, and light rotation measurements in an attempt to characterize these compounds. It was concluded that the lighter rare earth acid chelates H[Ln(EDTA)] contain a pentadentate EDTA molecule. Since the compounds studied all contained one mole of tightly bound water it was assumed that the hexacoordinated rare earth ion satisfied its sixth coordination position with water. The present paper is primarily an extension of Moeller's work which includes the entire series of rare earth chelates.

Experimental

Preparation of the Acids H[Ln(EDTA)].—The rare earth oxides used in the preparation of the chelate compounds were supplied by the rare earth separation group at the Ames Laboratory of the Atomic Energy Commission. All of the oxides were of 99.9% or greater purity as determined by emission spectroscopy. Each rare earth oxide was dissolved in hydrochloric acid and the excess acid was removed by evaporation to incipient dryness. The rare earth chloride obtained was used to saturate a cation-exchange column and the column then was eluted with a 5-g. per l. solution of the triammonium salt of EDTA (Geigy Chemical Co.). A dilute solution of eluant was necessary to avoid precipitation of the sparingly soluble H[Ln(EDTA)] compounds in the interstices of the resin bed. The eluate collected from the column contained H[Ln(EDTA)], which was induced to precipitate by concentration of the eluate solution by evaporation. The metal contents of the individual acidic chelate compounds were determined by direct ignition of the chelates to the corresponding rare earth oxides. Apparent formula weights, based on the metal assay, were calculated from the weights of the respective samples and oxide residues. From the apparent formula weights empirical formulas were inferred from the reasonable assumption that rare earth, EDTA anion, and water were combined in the ratio 1:1:*n*.

Preparation of K[Ln(EDTA)] and NH₄[Ln(EDTA)].—The potassium and ammonium salts were obtained either by direct neutralization of the chelate acids or by direct reaction in water of rare earth oxide, EDTA acid, and the proper hydroxide in the mole ratio of 0.5:1:1.⁵ The ammonium salts were crystallized directly from water. The potassium salts were crystallized by first concentrating their

solutions and then adding acetone with stirring. The ammonium salts were assayed for rare earth by direct ignition to the rare earth oxides, but neither this method nor the oxalate precipitation method was applicable to potassium salts due to potassium interference. The potassium salts were assayed for rare earth by completely decomposing the chelates by digestion with a nitric acid-perchloric acid mixture and titrating the residues chelometrically with EDTA.⁶

Determination of Acid Ionization Constants.—The ionization constants of the acids H[Ln(EDTA)] were determined at 20° by titration of the acids with standardized carbonate-free potassium hydroxide prepared by the method of Powell and Hiller.⁷ The ionic strength of the solutions was kept at 0.015 using potassium nitrate. Hydrogen ion concentrations were determined by pH measurements made with a Beckman Model G pH meter. The measurements were taken at pH values high enough to permit us to neglect the dissociation of the chelate itself in calculating the ionization constants.

Infrared Spectra.—Infrared spectra of the acids H[Ln(EDTA)] were recorded using a Perkin-Elmer Model 13 spectrophotometer equipped with calcium fluoride prisms. The solid chelates were pressed into disks using potassium bromide as a diluent. Approximately 1 mg. of chelate was used in each disk.

X-Ray Powder Patterns.—Diffraction patterns were obtained using a Norelco Debye-Scherrer type camera with a 57.3-mm. radius. Copper K α radiation was used.

Results and Discussion

When the chelates H[Ln(EDTA)] were precipitated from water and dried in air, the amount of water present was found to be dependent on the humidity of the air as well as the temperature. When these chelates were dried at 110° for 24 hr., two types of complexes were found. Those containing cerium, praseodymium, neodymium, and samarium retained one mole of water per mole of chelate; those containing the remaining rare earths became anhydrous. Thermobalance studies made on the monohydrated light rare earth chelates revealed that the water was strongly associated with the chelate molecule and was not released until the chelate itself decomposed. It is reasonable, therefore, to assume that this tightly bound water occupies one of the coordination positions of the central rare earth ion. Such an assumption is in accord with previous work performed with the neodymium and samarium compounds.⁴ Thus it appears that the acid chelates of cerium, praseodymium, neodymium, and samarium contain a pentadentate EDTA molecule in the solid state. An explanation of the nature of the EDTA molecule in the anhy-

(3) (a) H. Brintzinger, H. Thiele, and U. Muller, *Z. anorg. allgem. Chem.*, **251**, 285 (1943); (b) H. Brintzinger and S. Munkett, *ibid.*, **256**, 285 (1948).

(4) T. Moeller, F. A. J. Moss, and R. H. Marshall, *J. Am. Chem. Soc.*, **77**, 3182 (1955).

(5) J. K. Marsh, *J. Chem. Soc.*, 1819 (1950); 1461, 3057 (1951); 4804 (1952).

(6) R. W. Schmid and C. N. Reilly, *J. Am. Chem. Soc.*, **78**, 5513 (1956).

(7) J. E. Powell and M. A. Hiller, *J. Chem. Educ.*, **34**, 330 (1957).

drous group of rare earth chelates is not arrived at so easily. If we assume that the acidic hydrogen blocks one of the carboxyl groups from coordination, then it is difficult to explain why the central rare earth ion does not satisfy its sixth coordination position with water in all cases. On the other hand, if we assume that EDTA satisfies all six coordination positions of the lanthanon ion we are left with a free proton in the molecule. Information relative to this problem was obtained from the infrared spectra of the chelate compounds.

The infrared spectra of $H[Sm(EDTA)]$ and $H[Eu(EDTA)]$ are shown in Fig. 1 and 2. The

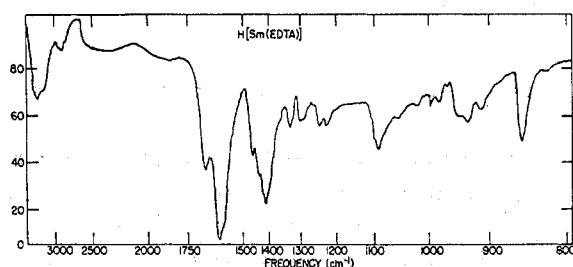


Fig. 1.—Infrared spectrum of monohydrate rare earth chelate.

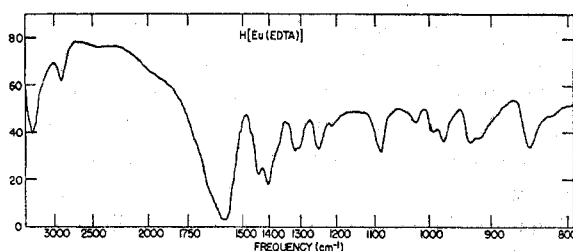


Fig. 2.—Infrared spectrum of anhydrous rare earth chelate.

absorption bands of all the compounds up to and including $H[Ho(EDTA)]$ are listed in Table I. The spectra of the erbium, thulium, ytterbium, and lutetium compounds also were obtained and were similar to that of the holmium compound. Table I contains only those bands obtained using calcium fluoride prisms in the infrared spectrophotometer. These prisms were chosen to give better resolution in the absorption region associated with the carboxyl group. The spectra shown in Fig. 1 and 2 were obtained using sodium chloride prisms.

The carbonyl stretching frequency in a normal $-COOH$ group occurs in the 1700-cm.^{-1} region of the spectrum. Table I shows that the acid chelates of cerium, praseodymium, neodymium, and samarium have an absorption band in the

TABLE I^a
PRINCIPAL ABSORPTION BANDS OF THE COMPOUNDS
 $H[Ln(EDTA)]$

| $H[Ln(EDTA)]$ | $-COOH$ | $-COO-$ (antisym.) | $-COO-$ (sym.) | $-COO-$ (sym.) | $-COO-$ (sym.) |
|---------------|---------|-----------------------|-------------------|-------------------|-------------------|
| Ce | 1667 | 1600 | 1416 | 1439 | 1460 |
| Pr | 1669 | 1600 | 1417 | 1439 | 1459 |
| Nd | 1670 | 1600 | 1418 | 1440 | 1459 |
| Sm | 1670 | 1600 | 1422 | 1440 | 1460 |
| Eu | | 1600 | 1408 | 1443 | |
| Gd | | 1600 | 1416 | 1445 | |
| Tb | | 1600 | 1411 | 1445 | |
| Dy | | 1600 | 1414 | 1446 | |
| Ho | | 1600 | 1417 | 1445 | |

^a Absorptions are reported in cm.^{-1} .

1670-cm.^{-1} region which is attributed to a highly associated $-COOH$ group in the chelate molecule. The $-COOH$ groups in the free $H_4(EDTA)$ absorb at 1690 cm.^{-1} . It seems reasonable to say that the acid chelates of cerium, praseodymium, neodymium, and samarium have one carboxyl group which is prevented from coordinating by the presence of the acidic hydrogen. This configuration is in accord with the thermobalance studies noted above and with previous work done on several of these compounds.⁴

It will be noted from Fig. 2 and Table I that the band observed in the light rare earth chelates at 1670 cm.^{-1} is completely absent in the heavier rare earth chelates. All attempts to resolve a band in this region failed. An examination of Fig. 2 shows that the very broad band in the 1600-cm.^{-1} region extends well into the 1670-cm.^{-1} region. However, the presence of a band at 1670 cm.^{-1} still would be detected if it were present. It should be mentioned, perhaps, that a comparison of the spectrum of Fig. 2 with those obtained by Sawyer and McKinnie shows that the two are similar even though these workers investigated only the sodium salts of EDTA metal chelates.⁸ If the interpretation of the infrared spectra of these heavy rare earth chelates is correct then it must be concluded that there is no $-COOH$ group present in these chelate molecules. Again assuming a hexacoordinated central rare earth ion, the EDTA molecule in these anhydrous acidic rare earth chelates would be hexadentate. That this type of structure is not only possible but may be quite common in acid chelates has been shown by Smith and Hoard.⁹ These workers have made a complete X-ray analysis of the solid

(8) D. T. Sawyer and J. M. McKinnie, *J. Am. Chem. Soc.*, **82**, 4191 (1960).

(9) G. S. Smith and J. L. Hoard, *ibid.*, **81**, 556 (1959).

dihydrogen ethylenediaminetetraacetatoaquonickel(II) chelate ($H_2[Ni(EDTA)] \cdot H_2O$). In this compound they found the EDTA to be pentadentate even though two acidic hydrogens were present in the molecule. One of the hydrogens is attached to a carboxyl group which thus is blocked from coordination. Smith and Hoard have inferred from packing relations that one of the uncomplex oxygens of a complexed carboxyl group carries the free hydrogen. The same structure has been assigned to the chelate $H_2[Cu(EDTA)] \cdot H_2O$ from the isomorphism of this chelate with the nickel chelate. Unfortunately a comparison of the infrared spectra of these compounds with the heavy rare earth chelates cannot be made, since the divalent metal compounds have a $-COOH$ group present. Apparently the heavy rare earth chelates of EDTA are also examples wherein hydrogen does not prevent a carboxyl group from bonding to the central atom.

The antisymmetric carbonyl vibrations of the complexed carboxyl groups are listed at 1600 cm.^{-1} in Table I. All are extremely broad and very intense. Therefore, measurements of this band could not be made with any degree of accuracy. There is no doubt that several different absorptions are occurring in this region, but they cannot be resolved. On the basis of resonance theory, the resonance occurring in a carboxyl group increases as the bond between the carboxyl group and a metal ion becomes more ionic. An increase in resonance imparts greater single bond character to the carbonyl oxygen and leads to a lowering of its absorption frequency. The low frequency of absorption observed for these groups is an indication that considerable resonance is present in the carboxyl group.

Sawyer has reported that the symmetric vibrations of complexed carboxyl groups occur in the $1350\text{--}1450 \text{ cm.}^{-1}$ region.¹⁰ The bands in this region are listed in Table I and have been assigned to the symmetric stretching vibrations. It should be emphasized, however, that there is no justification for assuming that these are the only bands due to the symmetric vibrations. Evidence for a change in structure in the series of rare earth chelates also is observed in this region. The monohydrated members exhibit three absorption bands, while the anhydrous members show only two bands. The bands in this region are quite sharp.

Metal-EDTA chelates consist of a central

TABLE II
OBSERVED *d*-SPACINGS OF THE COMPOUNDS
 $H[Ln(EDTA)]$

| Compound | <i>d</i> -Spacings |
|--------------------------|----------------------|
| $H[Nd(EDTA)] \cdot H_2O$ | 5.89 vs ^a |
| | 4.91 w |
| | 4.38 vvw |
| | 3.94 s |
| $H[Sm(EDTA)] \cdot H_2O$ | 5.83 vs |
| | 4.88 w |
| | 4.35 vvw |
| | 3.93 s |
| $H[Eu(EDTA)]$ | 5.70 s |
| | 4.68 vs |
| | 4.18 vvw |
| | 3.82 w |
| $H[Gd(EDTA)]$ | 5.62 s |
| | 4.60 vs |
| | 4.16 vvw |
| | 3.79 w |

^a vs-very strong, s-strong, w-weak, vvw-very very weak.

metal ion that is essentially completely engulfed by the organic chelating agent. Therefore, relations between adjoining molecules in the crystal should be dependent on the configuration of the EDTA molecule surrounding the metal ion. For a series of chelates of similar metal ions such as the rare earths one might suspect that, if the EDTA molecule is similar in all of the compounds, the solids should have isomorphous structures. The changes in structure of the $H[Ln(EDTA)]$ chelates noted above should be accompanied by corresponding changes in the packing of molecules in the chelate crystals. This would suggest that the crystalline solids should exhibit two series of isomorphous compounds. The chelates from cerium to samarium should be mutually isomorphous but not isomorphous with the chelates from europium through lutetium. X-Ray diffraction patterns of the entire series of compounds have been recorded and the above is shown to be true. Table II lists the *d*-spacings in Å. calculated for several of the lines of the neodymium, samarium, europium, and gadolinium chelates. The patterns of the cerium and praseodymium compounds are similar to those of neodymium and samarium while the patterns of the heavy members are similar to those of europium and gadolinium. Many more lines than those listed were observed in the patterns but only a few have been used for illustration.

It can be seen at this point that thermal decomposition, infrared absorption, and X-ray diffraction studies all show that there is a change

in the structure of the solid chelates $H[Ln(EDTA)]$. Infrared studies suggest that the change corresponds to a change in the EDTA anion from a pentadentate to a hexadentate configuration. Whether or not such a change occurs in solution is another problem. First of all, the solid compounds were studied after they had been dried at 110° . Secondly, the change in environment from solid to solution may well be accompanied by a change in the nature of the molecule. There is little doubt that EDTA chelates are stabilized by hydrogen bonding in solution. Four carbonyl oxygens available for hydrogen bonding certainly should influence the properties of the molecule in solution. Effects due to hydrogen bonding would seem highly likely in view of the strain present in a hexadentate EDTA chelate.¹¹

The acid dissociation constants have been determined roughly by a potentiometric method and their values are listed in Table III. The constants of the cerium and praseodymium chelates have been omitted due to the low solubility of these compounds. The determination of the constants was hindered by the strength of the acids and the necessity of measuring small hydrogen ion concentrations so that dissociation of the chelates could be neglected. For this reason the pK_{ion} values are reported only to the first decimal place. It is evident from Table III

TABLE III
IONIZATION CONSTANTS OF THE COMPOUNDS
 $H[Ln(EDTA)]$

| $H[Ln(EDTA)]$ | pK_{ion} | $H[Ln(EDTA)]$ | pK_{ion} |
|---------------|------------|---------------|------------|
| Nd | 2.5 | Dy | 2.8 |
| Sm | 2.6 | Ho | 2.7 |
| Eu | 2.6 | Er | 2.8 |
| Gd | 2.7 | Tm | 2.6 |
| Tb | 2.6 | Yb | 2.7 |
| | | Lu | 2.5 |

that little change in the ionization constant of the acid chelate occurs across the series of rare earths. This would seem to indicate that the anion $[Ln(EDTA)]^-$ in solution is similar throughout the series.

Studies of the ionic salts of the $[Ln(EDTA)]^-$ anion should be more indicative of its nature in solution than a study of the solid acids. The presence of an acidic hydrogen in the EDTA chelates does not permit an *a priori* assumption of a carboxyl group blocked from coordination.⁸

Nevertheless, the presence of an acidic hydrogen certainly constitutes a driving force tending to change the coordination number of the EDTA anion. This has been shown to be the case for the Co(III)-EDTA chelates.^{12,13} Thus, it may be that ionic salts of $[Ln(EDTA)]^-$ are similar in structure even though their acids are not.

Brunisholz has reported on the hydrates of the ammonium and potassium salts of rare earth chelates of EDTA.¹⁴ These compounds crystallize directly from water with eight moles of water per mole of chelate. The authors of this article have found that salts having the form $K-[Ln(EDTA)] \cdot H_2O$ can be obtained by neutralization of the acids, concentration of the resulting solution by evaporation, and addition of acetone with stirring. The resulting precipitate, dried at 110° for 24 hr., yields the monohydrate. No change in hydration is noted across the rare earth series. Thermal decomposition studies of these salts revealed that the hydrate water is not evolved before decomposition of the compound occurs. Since we are dealing with ionic salts, the postulation of a pentadentate EDTA species based on these results is weak. The fact that all the chelate salts are monohydrated is of greater significance than the fact that they cannot be completely dried. It may be that the water serves as a bridge between the chelate anion and the potassium cation rather than being in the coordination sphere of the rare earth ion. More definite information could be obtained from X-ray diffraction patterns of these salts; however, all of the diffraction patterns obtained at this Laboratory had very dark backgrounds and the lines were impossible to characterize. Other workers have had similar difficulties with several rare earth chelates crystallized from alcohol.¹⁵ An attempt was made to obtain patterns from the ionic salts which first were crystallized from water and then dried at 110° for 24 hr. The ammonium salts were chosen for this purpose. The powder patterns obtained after drying, however, were not much better than those obtained with the potassium salts. Comparison of the patterns of the dried neodymium and gadolinium compounds showed that the two probably were isomorphous but the patterns were such

(12) M. L. Morris and D. H. Busch, *J. Am. Chem. Soc.*, **78**, 5178 (1956).

(13) H. A. Weakliem and J. L. Hoard, *ibid.*, **81**, 549 (1959).

(14) G. Brunisholz, *Chimia*, **11**, 97 (1957).

(15) T. Moeller and E. P. Howitz, *J. Inorg. Nucl. Chem.*, **12**, 49 (1959).

(11) R. L. Pecsok, *J. Chem. Educ.*, **29**, 597 (1952).

that it did not appear worthwhile to run the entire series. It is interesting to note that the octahydrated sodium salts of praseodymium, neodymium, samarium, and gadolinium are isomorphous.⁴

Acknowledgments.—The authors would like to

express their gratitude to H. R. Burkholder for the preparation of the compounds and the thermo-balance studies which were reported in this article. The authors also are indebted to the infrared spectroscopy group of the Ames Laboratory of the Atomic Energy Commission for recording the infrared spectra.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Complexes of the Rare Earths. I. Iminodiacetic Acid

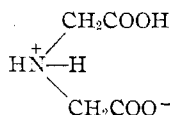
By LARRY C. THOMPSON

Received October 27, 1961

Stepwise stoichiometric formation constants have been determined for the complexes of the rare earths (including yttrium) with iminodiacetic acid. The measurements have been made in aqueous solutions of ionic strength $\mu = 0.1$ (KNO_3) and a temperature of 25° . Trends in the values of $\log K_1$ and $\log K_2$ are discussed, and $\log K_1$ is further compared to the similar values for the dipicolinic acid chelates.

Although the chelating tendencies of the trivalent rare earth ions have been investigated for many multidentate aminopolycarboxylic acids,¹⁻⁶ relatively few studies have been carried out with simpler ligands which form other than 1-1 chelates. In order to obtain a clearer understanding of the factors which influence the formation and stability of rare earth chelates, it is imperative that such ligands be investigated. The stepwise formation constants thus obtained can yield information as to steric effects and the relative ability of the rare earth ions to coordinate to different functional groups.

Such a project has been undertaken in this Laboratory, and the formation constants for the rare earth-iminodiacetic acid (IMDA) chelates are reported here.



(1) For a survey of the literature up to May, 1960, see L. C. Thompson, Ph.D. Dissertation, University of Illinois, 1960.

(2) J. L. Mackey, Ph.D. Dissertation, Iowa State University of Science and Technology, 1960.

(3) G. Anderegg, *Helv. Chim. Acta*, **43**, 825 (1960).

(4) I. Grenthe and W. C. Fernelius, *J. Am. Chem. Soc.*, **82**, 6258 (1960).

(5) I. Grenthe, *ibid.*, **83**, 360 (1961).

(6) A. Sonesson, *Acta Chem. Scand.*, **14**, 1495 (1960).

Experimental

Solutions.—A carbonate-free potassium hydroxide solution was prepared from a Fisher standard and standardized against potassium phthalate. IMDA obtained from the Dow Chemical Co. was purified by two recrystallizations from distilled water. An approximately 0.005 *M* solution was prepared and standardized by acidimetric titration both in the absence and presence of a slight excess of copper(II). A 1.000 *M* potassium nitrate solution was prepared from the analytical reagent.

Approximately 0.005 *M* rare earth nitrate solutions,⁷ with the exception of cerium, were prepared by dissolving a weighed amount of the oxide (99.9% pure) in a known excess of standard nitric acid. A cerium(III) nitrate solution was prepared from cerium(III) nitrate hexahydrate. The rare earth content of each solution was determined by a complexometric titration using EDTA and Eriochrome Black T.⁸ In addition, the cerium, neodymium, and samarium solutions were analyzed by precipitation as the oxalates, igniting to the oxides, and weighing. In all cases the experimental concentrations were found to be in good agreement with that calculated from the weight of oxide used. The excess nitric acid was found by adding an equivalent amount of the rare earth solution to a standard $\text{Na}_2\text{H}_2[\text{EDTA}]$ solution and titrating the hydrogen ions. Good agreement between the experimental and calculated values was found.

Experimental Procedure.—The experimental procedure

(7) The rare earth materials were generously supplied by Lindsay Chemical Division, American Potash and Chemical Corp., West Chicago, Illinois.

(8) G. Schwarzenbach, "Complexometric Titrations," trans. by H. Irving, Interscience Publishers, Inc., New York, N. Y., 1957, p. 73.