chloride complex at 20° and ionic strength 1.00. They found some slight indication of a second complex under their conditions, but their highest chloride concentration was 0.5 *M*. They suggested that this effect might be attributed to a change in activity coefficients as well as to the formation of a second complex. In our experiments the medium was changed from 2.0 *M* in perchlorate to 2.0 *M* in chloride ion. The effect here may have been brought about by differences in the rate of change of activity coefficients with increase in chloride concentration at different temperatures. If such is the case, better estimates of the values for the formation of UCl^{+3} would be obtained from the data at lower chloride concentrations. These have been estimated as: 1.5 at 40°, 1.8 at 25° and 3.3 at 10°. These values show a consistent change with change in temperature, but are only approximate.

Betts and Leigh[1] reported values of 338 and 250 for the stability constants of the first and second uranium(IV) sulfate complexes at 25° (for the reactions as written in Table II). Sullivan and Hindman,[2] in their recalculation of the data of Betts and Leigh, obtained values for these constants of about 260 and 5400.[7] The values obtained here are somewhat higher than these recalculated values. The first constant is more in line with the original values reported by Betts and Leigh but the results do bear out the contention of Sullivan and Hindman that the second constant is much higher than the value reported by Betts and Leigh. The results here were corrected, by successive approximations, for the amount of complexing agent used up in the reaction.

The results found here for thiocyanate complexes at 25° compare favorably with those of Ahrland and Larsson[3] at 20° and ionic strength 1.00. These workers reported values of 31 and 90 for the first two complexes and an approximate value of 150 for the third complex. They pointed out, however, that they could not definitely prove the existence of the third complex.

Several attempts were made to measure the stability of complexes of uranium(IV) and fluoride ions. Under our usual experimental conditions extremely high distribution ratios were obtained even with low fluoride concentrations. By increasing the TTA concentration to 0.500 *M* a reasonable amount of extraction did occur, but it was not then possible to back-extract uranium(IV) from the aqueous phase. By taking the aqueous phase concentration by difference between the original and final count of the benzene phase, a rough estimate was made of the magnitude of the fluoride constants at 25°. For the reactions written

$$U^{+4} + HF = UF^{+3} + H^{+}$$
$$U^{+4} + 2HF = UF_2^{+2} + 2H^{+}$$

(no third complex was considered), the first constant was of the order of 10^6 and the second of 10^8. No account was taken of the decrease in fluoride concentration by complex formation, so these values should undoubtedly be even higher.

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(7) For the reaction written

$$USO_4^{++} + HSO_4^{-} = U(SO_4)_2 + H^{+}$$

the value reported by Betts and Leigh is 0.74 and by Sullivan and Hindman about 21. Our value is about 22.

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Observations on the Rare Earths. LXVI.[1] Some Characteristics of Ethylenediaminetetraacetic Acid Chelates of Certain Rare Earth Metal Ions[2]

BY THERALD MOELLER, FRANK A. J. MOSS AND ROBERT H. MARSHALL

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Reaction of oxides of tripositive rare earth metal ions with ethylenediaminetetraacetic acid has been used to prepare moderately strong acids of the type $H[Ln(enta)] \cdot xH_2O$ and salts of the type $Ln[Ln(enta)]_3 \cdot yH_2O$. Inclusion of sodium hydroxide in the reaction yields salts of the type $Na[Ln(enta)] \cdot zH_2O$, and reactions of the acids with alkaloids give corresponding alkaloid salts. These compounds have been characterized and related to each other by the physicochemical techniques of *p*H titration, ion migration, X-ray diffraction and differential thermal analysis. Infrared spectra have been interpreted as showing that in species containing the group $[Ln(enta)]^-$ ethylenediaminetetraacetate occupies only five coördination positions and possesses an uncomplexed carboxyl group. Lack of resolution of the potentially asymmetric species $[Y(enta)(H_2O)]^-$ suggests that the bonding is not highly covalent in this ion. Fractional separations of the rare earth elements based upon precipitation of the acids $H[Ln(enta)] \cdot xH_2O$ or crystallization of the sodium salts of these acids are suggested.

Introduction

Since the isolation of the ethylenediaminetetraacetic acid (abbreviated hereinafter H_4enta) derivatives LaH(enta), NdH(enta), and $Y_4(enta)_3 \cdot 24H_2O$ by Brintzinger and co-workers,[3,4] the bulk of the published information upon rare earth metal–enta compounds has dealt with the properties of their solutions. Thus, it has been shown that neodymium and enta ions react in solution in a 1:1 stoichiometry,[5] that the presence of enta profoundly affects the absorption spectra of certain rare earth metal ions,[5–7] and that improved separations of the

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(1) For the preceding paper in this series, see T. Moeller and M. Tecotzky, THIS JOURNAL, **77**, 2649 (1955).

(2) Based upon the doctoral dissertations of F. A. J. Moss, 1952 and R. H. Marshall, 1954, University of Illinois.

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rare earth metal ions by precipitation procedures[8–10] and by ion-exchange techniques[11–15] can be effected in the presence of enta materials. Furthermore, the stabilities of the 1:1 complexes in solution with respect to their components have been shown to increase markedly with decreasing size of tripositive rare earth metal ion present.[16,17] Although existence of complex anions of the type $[Ln(enta)]^-$ (Ln = rare earth element or yttrium) is well established,[5,8,17] descriptions of isolated compounds have been limited to a few observations on substances of the types HLn(enta) and $Na[Ln(enta)]\cdot 6H_2O$[3,7,8] and a single observation upon the material $Y_4(enta)_3\cdot 24H_2O$.[4]

Investigations designed to systematize these observations have led to the conclusion that the fundamental complexes formed are acids of the type $H[Ln(enta)]\cdot xH_2O$ and that other materials are salts of these acids. Reactions leading to both the acids and their salts have been studied, and the compounds obtained have been characterized by various physicochemical techniques. In studies to determine the nature of the bonding in these species, the infrared spectra of a number of the compounds have been measured for the first time, and attempts have been made to resolve the potentially asymmetric $[Y(enta)(H_2O)]^-$ ion.

Experimental

Materials Used.—Rare earth materials—from the University of Illinois stocks—were of 98% to atomic weight purity and were obtained as oxides. These were ignited and cooled just prior to use. Samples of high purity ethylenediaminetetraacetic acid were kindly provided by the Alrose Chemical Company and by Versenes, Inc. All other materials were of analytical reagent quality and were used without further purification.

Preparation of Acids $H[Ln(enta)]\cdot xH_2O$ and their Inorganic Salts.—Although a solid, NdH(enta), had been obtained[3] by evaporation of solutions containing neodymium chloride and ethylenediaminetetraacetic acid, the product was contaminated with chloride. This difficulty is obviated by direct reaction of the acid with aqueous suspensions of the oxides of the tripositive elements in 1:1 mole ratios of H_4enta to Ln^{+3}. Reaction occurs at room temperature upon stirring the suspensions and yields slightly opalescent solutions which are clarified by filtration. A typical reaction involved 8.76 g. of the acid H_4enta and 5.04 g. of neodymium oxide in 200 ml. of water. Oxides of the tripositive elements (including yttrium) studied reacted readily: the oxides CeO_2 and Pr_6O_{11} oxidized the "enta" acid. Solutions obtained with cerium group materials (*e.g.*, neodymium, samarium), either upon standing at room temperature for several days or upon being heated on the steam-bath for several hours, deposited finely-divided, dense, crystalline precipitates with acidic properties, which after washing could be dried at 110° without decomposition. With yttrium, however, no precipitation was noted, but crystallization was effected by evaporation. Differences in crystallization rates may make these materials useful for fractional separations. The dried products were analyzed for carbon, hydrogen and nitrogen by microanalytical techniques and for rare earth metal contents by ignition to oxides. *Anal.* Calcd. for H[Ln(enta)]: atom ratios C, 10.0; H, 13.0; N, 2.0; Ln, 1.0. Found for neodymium complex: atom ratios C, 10.0, 10.03; H, 17.4, 16.4; N, 2.05, 1.96; Nd, 1.0, 1.0. Found for samarium complex: atom ratios C, 9.8, 9.8; H, 17.1, 16.0; N, 1.91, 1.92; Sm, 1.0, 1.0. Found for yttrium complex: atom ratios C, 9.26, 9.67; H, 16.2, 15.8; N, 1.73, —; Y, 1.0, 1.0. These data are consistent with formulations as 1 Ln:1 enta complexes, but the hydrogen analyses suggest variable water contents. In no case were analytical data indicative of formation of a completely anhydrous product. These results and other properties suggest the formulation $H[Ln(enta)]\cdot xH_2O$.

Solutions remaining from reactions of neodymium and samarium oxides bore the characteristic colors of the rare earth metal ions, but deposited no additional products upon evaporation to viscous sirups. Desiccation of these sirups gave glass-like solids. The same products were obtained by addition of equal volumes of ethanol to the viscous sirups. Although neodymium and samarium materials were easily obtained, in only one instance could a comparable yttrium compound be produced. *Anal.* Calcd. for $Ln[Ln(enta)]_3$: atom ratios C, 7.5; H, 9.0; N, 1.5; Ln, 1.0. Found for neodymium complex: atom ratios, C, 7.53; H, 17.5; N, 1.6; Nd, 1.0. Found for samarium complex: atom ratios, C, 7.37; H, 11.1; N, 1.48; Sm, 1.0. These data, together with the properties of the materials, are consistent with the formulation $Ln[Ln(enta)]_3\cdot yH_2O$, hydrogen analyses for no compound being completely indicative of a constant number of water molecules. Anhydrous substances were not obtained.

Sodium salts were easily obtained by neutralizing the free acids H[Ln(enta)] with sodium hydroxide and evaporating to crystallization. A more convenient procedure is that of Marsh[8] in which the oxide of the tripositive element, ethylenediaminetetraacetic acid, and sodium hydroxide react in 0.5:1:1 mole ratio in boiling water. Evaporation after filtration gave well-formed crystals in each instance. With praseodymium, the oxide Pr_6O_{11} was first reduced with hydrazine hydrate[18] before reaction. Sodium salts of the complex acids of praseodymium, neodymium, samarium, gadolinium and yttrium were prepared and purified by recrystallization. Analyses were consistent with formulation as $Na[Ln(enta)]\cdot zH_2O$. Thus, for the neodymium compound: calcd. for Na[Nd(enta)]: atom ratios C, 10.0; H, 12.0; N, 2.0; Nd, 1.0; Na, 1.0. Found: atom ratios C, 10.5; H, 27.0; N, 1.91; Nd, 1.0; Na, 0.99; the extra hydrogen indicating the presence of water of hydration. Controlled acidification of solutions of the sodium salts of the cerium earth complex, followed by heating, gave the insoluble free acids. This is a more convenient preparational procedure than that previously outlined, but excess acid causes decomposition through precipitation of the free acid H_4enta.

Preparation of Alkaloid Salts.—Brucine, strychnine, quinine and cinchonine salts of the acids H[Nd(enta)] and H[Y(enta)] (selected as typical of the cerium and yttrium groups, respectively) were obtained by direct reactions of the free alkaloids with the acids in equimolecular quantities in aqueous solution and subsequent crystallization. The following directions for the brucine salt of the neodymium acid are typical: One hundred ml. of water was added to 1.866 g. (0.004 mole) of brucine and 1.734 g. (0.004 mole) of the acid H[Nd(enta)], and the suspension was heated until a clear solution resulted. The cooled and filtered solution was evaporated in a current of air to a pink, crystalline product. Crystalline substances were obtained in the brucine–yttrium and strychnine–yttrium systems only after addition of ethanol. The strychnine–neodymium, quinine–neodymium and cinchonine–neodymium compounds were obtained as glasses upon evaporation and then precipitated, after dissolution in water, by subsequent addition of ethanol and diethyl ether. The quinine–yttrium and cinchonine–yttrium compounds could be prepared only as gelatinous precipitates by addition of ethanol. The generally hygroscopic materials were dried at 110–120° prior to analyses. *Anal.* Calcd. for $C_{23}H_{26}O_4N_2\cdot H[Nd(enta)]$(brucine): C, 47.83; H, 4.74; N, 6.77. Found: C, 47.96; H, 5.03; N, 7.03. Calcd. for $C_{23}H_{26}O_4N_2\cdot H[Y(enta)]$: C, 51.26;

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H, 5.09; N, 7.25. Found: C, 51.96; H, 5.52; N, 7.42. Calcd. for $C_{21}H_{22}O_2N_2 \cdot H[Nd(enta)]$ (strychnine): C, 48.49; H, 4.60; N, 7.30. Found: C, 48.04; H, 4.92; N, 6.95. Calcd. for $C_{21}H_{22}O_2N_2 \cdot H[Y(enta)]$: C, 52.25; H, 4.95; N, 7.86. Found: C, 51.94; H, 5.21; N, 7.76. Calcd. for $C_{20}H_{24}O_2N_2 \cdot H[Nd(enta)]$ (quinine): C, 47.54; H, 4.92; N, 7.39. Found: C, 47.69; H, 4.97; N, 7.10. Calcd. for $C_{19}H_{22}ON_2 \cdot H[Nd(enta)]$ (cinchonine): C, 47.87; H, 4.85; N, 7.70. Found: C, 48.10; H, 5.10; N, 7.46.

Physicochemical Studies.—All *p*H measurements were made with a Beckman Model H *p*H Meter. Ion migrations were observed under an applied potential of 110 volts in an H-type cell fitted with bright platinum electrodes and a porous frit separating the two compartments. Differential thermal analyses were made with the apparatus of Professor R. E. Grim of the University of Illinois Geology Department, using calcined alumina as reference material. X-Ray diffraction patterns were obtained with a Picker industrial diffraction unit with chromium radiation. Infrared spectra were measured with a Perkin-Elmer Model 21 Double Beam Recording Spectrophotometer, using Nujol suspensions between rock salt plates. Light rotation measurements were made with a Schmidt and Haensch Polarimeter (No. 9143), using light of wave length 5893 A. (sodium-D line) and giving maximum mean deviations of 0.003°.

Attempted Resolution of Enta Complexes.—Because of the absorption characteristics of neodymium(III) in the sodium-D line region, optical rotation measurements on solutions of neodymium compounds were unreliable. Hence, only the colorless yttrium compounds were employed. Treatment of a 20-ml. volume of a solution containing 0.54 g. of the acid H[Y(enta)] as sodium salt with 1 g. of *d*-quartz[19] for 15 min., followed by filtration and observation in the polarimeter, gave a change in rotation of only 0.003°, a figure within the limits of experimental error.

Samples of the brucine, strychnine and quinine derivatives of the acid H[Y(enta)], obtained in each case by fractional precipitation with ethanol or with ethanol and diethyl ether, showed no changes in optical rotations in aqueous solutions over 2-hour periods and gave rotations strictly comparable with those characterizing their alkaloid contents. Qualitative removal of the alkaloid in each case by precipitation with excess potassium iodide–iodine solution, followed by removal of iodine with sodium sulfite, gave solutions differing in optical rotation from water blanks by no more than 0.003°. The data are all indicative that under the conditions outlined resolutions were not effected.

Discussion

The 1:1 and 4:3 Rare Earth Metal Ion:Enta Complexes.—Analytical data already summarized indicate the existence of two series of compounds characterized, respectively, by rare earth metal ion:enta mole ratios of 1:1 and 4:3. Although at first glance these might be regarded, respectively, as acid and normal salts of the acid H_4enta, their properties are not consistent with this view. The relationships between the two series may be shown by physicochemical data. Thus, *p*H titration studies on the 1:1 compounds show these substances to be acids of moderate strengths (*e.g.*, pK = *ca.* 3.7 for $H[Nd(enta)] \cdot xH_2O$) containing one gram atom of replaceable hydrogen per mole. Corresponding titrations of the 4:3 compounds give, after initial sharp increases in *p*H, precipitation of hydrous hydroxides at essentially constant *p*H. In the typical case of the neodymium compound, precipitation was found to be complete when just short of 0.2 of the alkali equivalent to the total neodymium present had been added, whereas the theoretical requirement for precipitation of one of the four neodymiums present per mole would be 0.25. However, since precipitation of neodymium hydroxide from other systems is apparently complete after addition of 0.63–0.86 of the theoretical quantity of hydroxyl ion,[20] it is logical to assume that in the 4:3 compounds one of the neodymium atoms present is not complexed and three are. The same reasoning may be extended to derivatives of the other elements. This is supported by ion migration studies on solutions of the 4:3 compounds which indicate almost immediate precipitations of hydrous hydroxides in the cathode compartment and show rare earth materials detectable by oxalate precipitation in the anode compartment. Comparable studies on the 1:1 complexes have shown the rare earth species to be anionic in nature.[5]

These data are in agreement with formulation of the 1:1 complexes as acids, H[Ln(enta)], any water of hydration being neglected, and of the 4:3 compounds as rare earth metal salts of such acids, $Ln[Ln(enta)]_3$. Further support of this view is given by the fact that the 4:3 compounds, both those containing but a single rare earth element and those containing two different rare earth metals, can be obtained by reaction of the 1:1 substances with oxides as

$$Ln_2O_3 + 6H[Ln(enta)] \longrightarrow 2Ln[Ln(enta)]_3 + 3H_2O$$

and that the 1:1 compounds can be prepared from the 4:3 substances by reaction with the acid H_4enta as

$$Ln[Ln(enta)]_3 + H_4enta \longrightarrow 4H[Ln(enta)].$$

X-Ray diffraction data on the species $H[Ln(enta)] \cdot xH_2O$, as summarized in Table I, show distinct similarities between the neodymium and samarium compounds but rather marked differences between these and the yttrium compound. Although all attempts to obtain crystalline $Ln[Ln(enta)]_3$ type compounds by slow evaporation, change in solvent, etc., failed, a single sample of the

TABLE I

SUMMARY OF X-RAY DIFFRACTION DATA ON *d*-SPACINGS

H[Nd(enta)] *d*, Å.	H[Sm(enta)] *d*, Å.	H[Y(enta)] *d*, Å.	$Nd[Nd(enta)]_3$ *d*, Å.	Na[Nd(enta)] *d*, Å.
13.10 (S)[a]	12.80 (S)	9.10 (VS)	12.40 (VS)	9.87 (VS)
7.38 (S)	7.32 (S)	6.59 (W)	8.08 (W)	8.83 (S)[b]
6.49 (MS)	6.43 (MS)	6.04 (W)	7.46 (VS)	7.78 (VS)
5.91 (VS)	5.86 (VS)	5.59 (W)	6.77 (W)	6.58 (MS)
4.89 (W)	4.85 (W)	5.34 (W)	6.23 (M)	5.86 (W)
3.96 (M)	3.95 (M)	3.76 (VW)	5.91 (MS)	5.69 (W)
3.75 (W)	3.72 (W)	3.16 (M)	5.42 (W)	4.93 (W)
3.61 (W)	3.53 (W)	2.86 (W)	4.81 (W)	3.91 (W)
3.18 (W)	3.15 (W)	2.61 (VW)	4.59 (VW)	3.72 (W)
3.06 (W)	3.04 (W)	2.43 (VW)	4.43 (W)	3.11 (MS)[b]
2.86 (W)	2.80 (W)	2.28 (VW)	4.11 (VW)	2.87 (VW)
2.70 (W)	2.60 (W)	2.18 (VW)	3.87 (VW)	2.74 (W)
2.64 (W)	2.62 (W)	2.03 (W)	3.74 (VW)	2.65 (W)
2.50 (VW)	2.48 (VW)	1.96 (VW)	3.62 (VW)	2.54 (VW)
2.45 (W)	2.44 (W)	1.74 (VW)	3.41 (VW)	2.30 (VW)
2.40 (VW)	2.39 (VW)		3.28 (W)	2.26 (VW)
2.09 (VW)	2.07 (VW)		3.00 (W)	2.08 (W)
2.04 (W)	2.02 (W)		2.87 (M)	1.98 (W)[b]
2.01 (VW)	2.00 (VW)		2.74 (VW)	1.91 (VW)
			2.69 (VW)	1.89 (VW)
			2.63 (W)	1.85 (VW)
			2.47 (W)	
			2.38 (VW)	
			2.25 (W)	
			2.07 (VW)	
			1.92 (VW)	
			1.91 (VW)	

[a] VS, very strong; S, strong; MS, medium strong; M, medium; W, weak; VW, very weak.
[b] Doublet.

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neodymium compound did crystallize in fine needles over a 9-month period. The X-ray diffraction pattern of this material (Table I) is somewhat different from that of the 1:1 acid. Heating at 110° rendered this sample amorphous to X-rays, and crystallization could not be effected again. The crystalline sodium salts, Na[Ln(enta)]·xH$_2$O gave excellent diffraction patterns, all of which were so nearly identical as to suggest complete isomorphism among these substances. Details of the pattern of the sodium salt containing neodymium are given in Table I, and pertinent comparative data for the compounds studied are summarized in Table II. The effects of the lanthanide contraction are apparent.

TABLE II

COMPARISON OF d-SPACINGS IN Na[Ln(enta)] TYPE COMPLEXES

Relative intensity[a]	Pr	Nd	Sm	Gd	Y
	d-spacings, Å.				
VS	9.89	9.87	9.87	9.84	9.77
S	8.87	8.83	8.81	8.81	8.76
VS	7.78	7.78	7.77	7.77	7.70
MS	6.58	6.58	6.52	6.49	6.48
MS	3.11	3.11	3.10	3.09	3.08

[a] VS, very strong; S, strong; MS, medium strong.

Some preliminary measurements on the water solubilities of salts of the type Na[Ln(enta)] at 25 ± 0.5°, as obtained by analyzing measured weights of solutions after equilibration for 48 hours, suggest the possibility of effecting useful separations through fractional crystallizations of these compounds. Solubilities, expressed as moles of anhydrous salt per 1000 g. of solution at 25°, are: Pr, 0.078; Nd, 0.072; Sm, 0.066; Gd, 0.079; Y, 0.334.

Nature of Bonding in [Ln(enta)]$^-$ Type Species.—The presence of six potential donor groups in the ethylenediaminetetraacetate structure suggests that this species may be sexadentate in its complexes. Indeed, such behavior has been more or less tacitly assumed in a number of instances,[21] although the presence of more than four chelate rings in the 1:1 cobalt(III)–enta complex in particular[22] and in other similar complexes in general[23] appears to be precluded by steric effects. The remaining coördination position of a 6-coördinate metal ion in a complex of the type 1 M:1 enta must then be filled either by a neutral molecule such as water or by an anion. This is found to be experimentally correct for the cobalt(III) materials.[22] If the tripositive rare earth metal ions are assumed to be 6-coördinate in their enta complexes, in keeping with their behaviors in say the β-diketone chelates, it is important to determine how many positions are filled by the ethylenediaminetetraacetate before any postulations regarding stereochemistry can be made.

Models of the Fisher–Hirschfelder type for a material of a 1 Ln:1 enta stoichiometry suggest that although either four or five coördination positions can be occupied without difficulty by the two nitrogens and, respectively, two or three carboxylic oxygen atoms of the enta group, the sixth can be filled by the fourth carboxyl only in a very highly strained arrangement. Although interpretations based upon such models are not conclusive, they are often indicative of true arrangements. Inasmuch as monobasic acids of the type H[Ln(enta)]·xH$_2$O and hydrated salts containing the corresponding uninegative anion have been characterized, it is not unreasonable to postulate the presence of one uncoördinated carboxyl group rather than two and to conclude that water is also included in the coördination sphere.

More definitive information may be expected from infrared data, particularly in view of the interpretation[24,25] of absorptions in the 1580–1650 cm.$^{-1}$ and 1690–1750 cm.$^{-1}$ regions as being due, respectively, to complexed and free carboxyl groups in the 1:1 cobalt(III)–enta complex. The spectra given in Figs. 1 and 2 may be interpreted similarly. The broad absorption in the 1690 cm.$^{-1}$ region for the acid H$_4$enta is due to C=O stretching in carboxyl groups partially associated through hydrogen bonding. The spectrum of the acid H[Nd(enta)] (actually a hydrate) shows the presence of at least two varieties of carboxyl group, the 1672 cm.$^{-1}$ band being due to C=O stretching in a partially associated –COOH group and the 1600 cm.$^{-1}$ band to C=O stretching in a complexed –COO$^-$ group. The relative intensities of the two absorptions are consistent with a conclusion that complexed carboxyl is present in the larger quantity. The somewhat similar, although less well defined, spectrum of the acid H(Y(enta)] indicates uncomplexed carboxyl at 1715 cm.$^{-1}$ and complexed carboxyl at 1610 cm.$^{-1}$ with a suggestion of associated but uncomplexed carboxyl at 1645 cm.$^{-1}$. Correspondingly, two types of carboxyl groups are also suggested by the spectra of the brucine salts of the two acids. On the other hand, the spectra of the salts Na[Nd(enta)], Na[Y(enta)] and Y[Y(enta)]$_3$ show only single broad C=O stretching bands in the 1605–1615 cm.$^{-1}$ region. These bands are too broad to permit conclusive determinations of types of carboxyl present, but it is not believed that their interpretation in terms of only complexed carboxyl[24] is clearly possible. On the bases of infrared data and chemical evidence, it is not unreasonable to conclude that only five coordination positions are occupied by the enta group.

The presence of water in all solid compounds isolated permits the assumption that the sixth coördination position is occupied by a water molecule. That water is an essential component of the structures is further suggested by differential thermal analysis data. Thus, for the hydrated H[Nd(enta)] acid, a dehydration step, beginning at 200°, involving the removal of firmly bonded water and leading directly to exothermic and endothermic decompositions of the organic portion of the material in the range *ca.* 300–800° was noted. With the hydrated Na[Ln(enta)] salts, dehydrations beginning below 100° were incomplete before decompositions began below 300°.

An [Ln(enta)(H$_2$O)]$^-$ group, as suggested by

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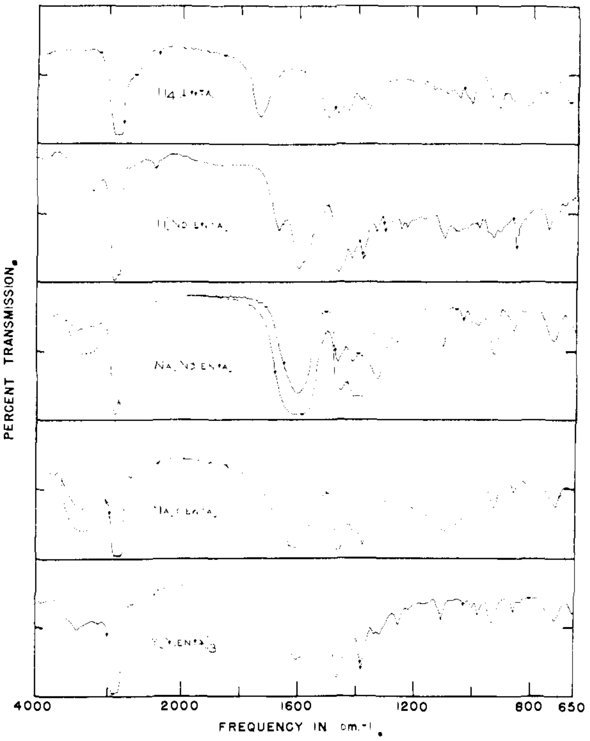

Fig. 1.—Infrared spectra of $[Ln(enta)]^-$ type compounds.

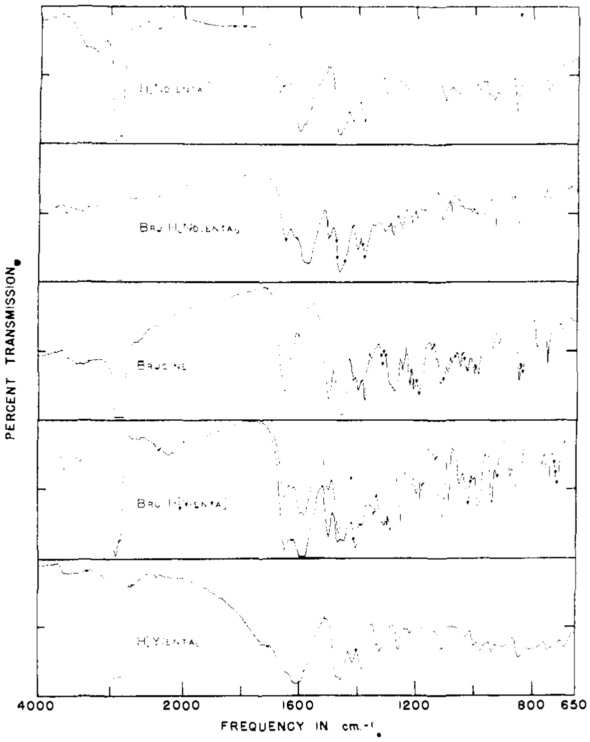

Fig. 2.—Infrared spectra of $[Ln(enta)]^-$ type compounds.

these considerations, should be asymmetric in an octahedral geometry and thus potentially capable of resolution providing the bonding present is sufficiently highly covalent in character. Inasmuch as complexes of this type give rather low equilibrium concentrations of Ln^{+3} ions,[17] a certain amount of covalency is undoubtedly present. However, the lack of any observed resolution by two methods of the species $[Y(enta)(H_2O)]^-$, where the presence of the comparatively small Y^{+3} material should enhance covalent character, suggests that even in this species sufficient covalency to maintain the rigid geometrical arrangement essential to asymmetry is probably absent. Such a conclusion is a reasonable one and is in agreement with the generally ionic characteristics of yttrium and rare earth metal salts.

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The Interaction of Chromium(III) and Chromium(VI) in Acidic Solution[1]

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It is observed that acidic solutions containing chromium(III) and chromium(VI) exhibit an enhanced absorbancy compared to that expected on the basis of no interaction. Measurements at 290 and 700 mμ demonstrate that the complexes responsible for this absorbancy enhancement contain one chromium(III) atom and one chromium(VI) atom. Studies as a function of the hydrogen ion concentration indicate that the complex species are $CrCrO_4^{+}$ and $CrCrO_4H^{++}$. These complex ions are not of sufficient stability to allow the evaluation of the equilibrium quotients for the reactions in which they are formed. Although the complexes form rapidly, it is believed that they are of the "inner-sphere" variety, the chromium(VI)-oxygen bond being broken and formed in the formation reaction. That is, the chromium(III)-chromium(VI) bonding involves an oxygen bridge Cr(III)-O-Cr(VI), the lability of the system being due to the high rate at which the chromium(VI)-oxygen bond can be formed and broken.

Although a number of investigators have reported the preparation of solid compounds containing chromium(III) and chromium(VI),[2-4] little attention has been devoted to the interaction of these two oxidation states in solution. In fact, little attention has been devoted to the complexes of any metallic cations and the chromium(VI) anionic species although a recent study of cerium(IV)-chromium(VI) complexes[5] has demonstrated that for cerium(IV), the chromate complex is more stable

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(1) This work has been supported in part by the United States Atomic Energy Commission.

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