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 thermobalance 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

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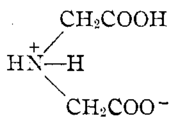
Stepwise stoichiometric formation constants have been determined for the complexes of the rare earths (including yttrium) with iminodiacetic acid. The measurements have been made in aqueous solutions of ionic strength $\mu = 0.1$ (KNO_3) and a temperature of 25°. Trends in the values of log K_1 and log 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 coördinate 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.



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 Na_2H_2[EDTA] solution and titrating the hydrogen ions. Good agreement between the experimental and calculated values was found.

Experimental Procedure.—The experimental procedure

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(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).

(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.

consisted of a potentiometric titration of IMDA alone and in the presence of the rare earth ions. In all cases the ionic strength was maintained at 0.1 by the addition of potassium nitrate. The runs were carried out in a constant temperature bath, the temperature of which was maintained at 25.00 ± 0.02°. A Beckman Model GS pH meter (used as a Model G) equipped with a calomel reference electrode and an all-purpose glass electrode was used to determine the pH values. The titration vessel was a 200-ml. Berzelius beaker fitted with a rubber stopper containing holes for the electrodes, microburet, and gas inlet and outlet tubes. Presaturated nitrogen obtained by bubbling commercial water-pumped nitrogen through 0.1000 M potassium nitrate solution was passed through the solution to effect stirring and to maintain an atmosphere free of carbon dioxide.

For reasons which are discussed below the solutions employed contained the IMDA and rare earth in the ratio of **5:1.**

Calculations.—Values of pH were converted to concentration values using the correction factor −0.08 pH unit found for a dilute solution of nitric acid. This correction was assumed to be valid in the pH range 3–10. The concentration of hydroxide ions was determined using a value of K_cw of 1.68×10^{-14}.[1] The acid dissociation constants were calculated by the method outlined by Chaberek and Martell.[9] The stability constants were calculated by solving simultaneous equations as developed by Block and McIntyre.[10]

Discussion

The values obtained for the IMDA dissociation constants are given in Table I. These can be compared with the literature values of 2.65 and 9.38 at 20°[11] and 2.54 and 9.12 at 30°.[9]

TABLE I

FORMATION CONSTANTS FOR IMDA–RARE EARTH CHELATES

$t = 25°$, $\mu = 0.1$ (KNO_3)

pk_1 = 2.58, pk_2 = 9.33

Metal ion	log K_1[a]	log K_2[b]
La^{3+}	5.88 ± 0.01[c]	4.09 ± 0.02
Ce^{3+}	6.18 ± .03	4.53 ± .02
Pr^{3+}	6.44 ± .03	4.78 ± .03
Nd^{3+}	6.50 ± .01	4.89 ± .01
Sm^{3+}	6.64 ± .02	5.24 ± .02
Eu^{3+}	6.73 ± .03	5.38 ± .03
Gd^{3+}	6.68 ± .01	5.39 ± .01
Tb^{3+}	6.78 ± .03	5.46 ± .04
Dy^{3+}	6.88 ± .02	5.43 ± .03
Ho^{3+}	6.97 ± .03	5.50 ± .03
Er^{3+}	7.09 ± .02	5.59 ± .01
Tm^{3+}	7.22 ± .02	5.68 ± .01
Yb^{3+}	7.42 ± .04	5.85 ± .03
Lu^{3+}	7.61 ± .03	6.12 ± .02
Y^{3+}	6.78 ± .03	5.25 ± .04

[a] K_1 = [Ln(IMDA)]/[Ln][IMDA]. [b] K_2 = [Ln(IMDA)$_2$]/[Ln(IMDA)][IMDA]. [c] 95% confidence limits.

In solutions in which the ratio of IMDA to rare earth ion was 1:1, a hydrolytic buffer region appeared. Even when the ratio was 2:1, this buffer region was present although it was much less pronounced, and in solutions containing a 3:1 mixture it had disappeared. When the 1:1 solution of neodymium was taken to pH 10 and allowed to stand, no visible precipitate was found to be formed. Rather, the solution became quite viscous and gelatinous, but remained clear. This behavior is contrary to that with nitrilotriacetic acid or hydroxyethyliminodiacetic acid,[12] both of which form more stable neodymium complexes than IMDA, and for both of which a hydrolytic buffer region is observed, followed by the formation of a distinct precipitate on standing. Consequently the solutions which were used for the determination of the formation constants contained a 5:1 ratio of IMDA to rare earth. In this way the complex formation curve was depressed toward lower pH values and hydrolysis was not evident in the titration. That there was no hydrolysis in the region which was studied also was shown by the fact that plots of $\bar{n}$ *vs.* pA (A = $IMDA^{-2}$) for varying ratios of IMDA and rare earth coincided within the experimental error.

Values of log K_1 for the IMDA chelates of some of the rare earths have appeared in the literature.[13] The value given in Table I for lanthanum is in good agreement with that reported previously, but the remaining values are approximately 0.3 to 0.4 log K unit lower than the previous values. In order to check the experimental technique, the values of log K_1 and log K_2 for the zinc–IMDA chelates were determined in a 5:1 solution. The values obtained at 25° ($\mu = 0.1$, KNO_3) were log $K_1 = 7.11$ and log $K_2 = 5.18$. These are in good agreement with the literature values of 7.03 and 5.14 at 30°.[9] In view of this, and the fact that values of the rare earth formation constants determined from data obtained from solutions having IMDA to neodymium or dysprosium ratios of 1:1, 2:1, 3:1, 5:1, and 10:1 were always in good agreement, it was concluded that the experimental approach was valid. We are puzzled by the disagreement with the values

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(9) S. Chaberek, Jr., and A. E. Martell, *J. Am. Chem. Soc.*, **74**, 5052 (1952).

(10) B. P. Block and G. H. McIntyre, Jr., *ibid.*, **75**, 5667 (1953)

(11) J. Bjerrum, G. Schwarzenbach, and L. G. Sillén, "Stability Constants," The Chemical Society, London, 1957, p. 23.

(12) Unpublished observations.

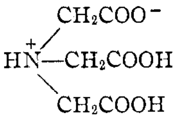
(13) R. Harder and S. Chaberek, *J. Inorg. Nucl. Chem* , **11**, 197 (1959).

previously reported and have no explanation for this difference.

The possibility of the existence of a complex higher than a 2:1 complex could not be eliminated. Values of $\bar{n}$ slightly higher than 2 were obtained in the 5:1 and 10:1 solutions but the errors inherent in measurements in basic solutions are such that the $\bar{n}$ values are unreliable and no satisfactory constants could be obtained.

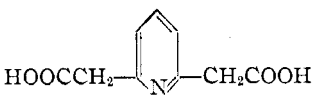
In general, the values of the formation constants show trends which have been noted before.[4] The usual discontinuity at gadolinium is observed in the log K_1 values. Since the yttrium chelate has the same log K_1 value as terbium, its position can be classified as "normal." [14]

The values of log K_1 parallel the similar values for the nitrilotriacetic acid (NTA)–rare earth chelates,[15] reflecting the similarity of the two chelating agents. A comparison of the structural formula of IMDA given above with that of NTA given below illustrates this similarity, and it is to be expected that the 1:1 chelates of these two ligands should differ only in the magnitude of log K_1.



$$\mathrm{H\overset{+}{N}(CH_2COO^-)(CH_2COOH)_2}$$

There does not appear to be any pronounced steric hindrance in the IMDA chelates since the log K_2 values do not show any decrease with the increasing atomic number of the rare earths. This is similar to the effect noted by Grenthe for the rare earth–dipicolinic acid (dipic) chelates.[5]



The trend found in log K_2 for the IMDA chelates is quite different from that found in the case of the 2:1 NTA–rare earth chelates in which steric hindrance is quite evident. The addition of a second IMDA or dipic ligand to the 1:1 chelate should not be accompanied by any steric repulsion since the ligands are relatively small and should fit easily into the structure. With NTA, however, the presence of the additional acetate group greatly increases the size of the molecule, and the 2:1 chelates should exhibit steric hindrance as the size of the rare earth ion decreases regardless of whether the coördination number is six or eight.[3]

The discontinuity at gadolinium occurs in the log K_2 values as well as the log K_1 values. Although the position of yttrium was classified as normal in the 1:1 chelate, there is a decided shift in its position based on the value of log K_2 which places it in the cerium-earth region. Since the over-all formation constant (log K_1 + log K_2) also shows that yttrium belongs in the cerium-earth group, this points up the necessity of more stepwise formation constant data before any generalizations can be made about the relationship of yttrium to the rare earths insofar as coördination tendencies are concerned. We have, at present, no explanation for the behavior of yttrium.

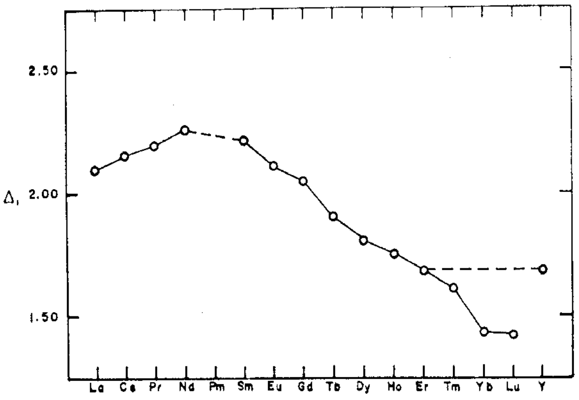


Fig. 1.—Δ_1 values (log $K_{1_{\text{Ln-dipic}}}$ − log $K_{1_{\text{Ln-IMDA}}}$) for the rare earth dipicolinate and iminodiacetate chelates.

Recently Anderegg[16] has suggested that the difference between the log K_1 values for dipicolinic acid chelates and the log K_1 values for iminodiacetic acid chelates should be positive for metals having large ionic radii, such as the alkaline earths. This effect was suggested on the basis of models which showed that the oxygen atoms of the carboxyl groups in dipicolinic acid could not get close enough to a small metal ion for the most effective chelation. An interesting test of this hypothesis is shown in Fig. 1 in which the values Δ_1 (log $K_{1_{\text{Ln-dipic}}}$ − log $K_{1_{\text{Ln-IMDA}}}$) are plotted against atomic number. If this hypothesis is correct, it would be expected that the value of Δ_1 should decrease as the atomic number increases (*i.e.*, the ionic radius decreases). The results given in the figure show that this is the case.

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[14] T. Moeller, L. C. Thompson, and R. Ferrús, in "Rare Earth Research," ed. by E. V. Kleber, The Macmillan Co., New York, N. Y., 1961, p. 3.

[15] G. Schwarzenbach and G. Anderegg, *Helv. Chim. Acta*, **39**, 1589 (1956).

[16] G. Anderegg, *ibid.*, **43**, 414 (1960).

Furthermore, the values of Δ_1 increase from lanthanum to neodymium and then decrease gradually, indicating that the first three rare earth ions are too large to allow the most effective enhancement of chelation.

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CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO, CHICAGO, ILLINOIS

α,β,γ,δ-Tetra-(4-pyridyl)-porphine and Some of its Metal Complexes

BY EVERLY B. FLEISCHER

Received December 20, 1961

A new porphyrin, α,β,γ,δ-tetra-(4-pyridyl)-porphine, has been synthesized and purified. The zinc, copper, and nickel complexes of this porphyrin have been prepared. The visible absorption spectra of these complexes were studied employing both chloroform and 1.0 *N* hydrochloric acid as solvents.

One of the limiting factors in the study of porphyrins and metalloporphyrins is their insolubility in aqueous solutions. Thus the study of the oxidation–reduction reactions of metalloporphyrins is hampered by their water insolubility.[1-3]

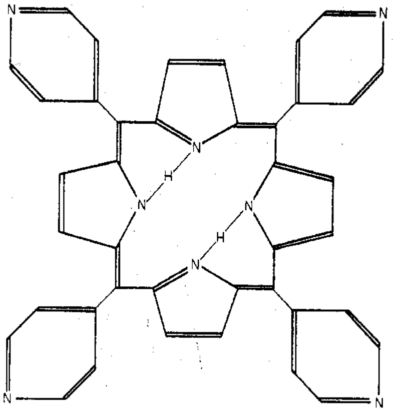

Fig. 1.—α,β,γ,δ-Tetra-(4-pyridyl)-porphine.

We have synthesized a new porphyrin, α,β,γ,δ-tetra-(4-pyridyl)-porphine, which is water soluble (Fig. 1). This porphyrin is a new member of the α,β,γ,δ-tetraphenylporphine series.[4]

The free base porphyrin can complex with metal ions to form metalloporphyrin complexes. The pyridines on α,β,γ,δ-tetra-(4-pyridyl)-porphine can pick up protons in acid solution; this property accounts for the porphyrin's water solubility.

In this communication we report the synthesis of α,β,γ,δ-tetra-(4-pyridyl)-porphine and some of its metalloporphyrin complexes and the spectral properties of these molecules.

Experimental

Synthesis.—Literature methods were used to make the α,β,γ,δ-tetra-(4-pyridyl)-porphine.[4] For the preparation of the zinc salt, 50 ml. of pyridine, 15 g. of zinc acetate, 25 ml. of pyrrole, and 35 ml. of 4-pyridine carboxaldehyde were mixed in a 250-ml. all-glass pressure bomb. The bomb was flushed with nitrogen and sealed. The reaction mixture was heated in an oil bath at 110° for 48 hr. Purple crystals of zinc-α,β,γ,δ-tetra-(4-pyridyl)-porphine were collected, washed with alcohol and ether, and dried in an oven at 110°. The yield was about 10%. There was more product dissolved in the reaction mixture but recovery was not attempted. The zinc derivative was purified on an alumina column (Fisher Alumina) using chloroform as a solvent and 5% methanol–chloroform as an eluent. The product was recrystallized from chloroform–methanol.

The porphyrin was prepared by removal of the zinc ion from the zinc porphyrin complex. The zinc derivative was dissolved in chloroform. To remove the zinc ion from the zinc porphyrin complex 6 *N* HCl was added to the chloroform solution. The porphyrin went into the acid layer as the diacid porphyrin. The free base porphyrin was extracted into chloroform after neutralization

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(1) J. F. Taylor, *J. Biol. Chem.*, **135**, 569 (1940).

(2) E. S. G. Barron, *ibid.*, **121**, 285 (1937).

(3) W. M. Clark, "Oxidation-Reduction Potentials of Organic Systems," Williams and Wilkins Company, Baltimore, Maryland, 1960, pp. 448–460.

(4) D. W. Thomas and A. E. Martell, *J. Am. Chem. Soc.*, **81**, 5111 (1959).