formation function for each metal with values of $\bar{n}$ calculated (circles and dots) from experimental values of [P′] and the over-all conditional formation constants.

Acknowledgment.—The authors wish to express their thanks to Dr. J. C. Sullivan of Argonne National Laboratory for providing the IBM 704 program for the least squares treatment of potentiometric titration data.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF
MINNESOTA AT DULUTH, DULUTH 18, MINNESOTA

Complexes of the Rare Earths. VI. N-Hydroxyethyliminodiacetic Acid

BY LARRY C. THOMPSON AND JUDITH A. LORAAS[1]

Received February 4, 1963

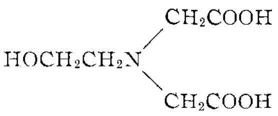
The formation constants of the complexes between the rare earth ions and N-hydroxyethyliminodiacetic acid (HIMDA) have been investigated at 25° and $\mu = 0.1$ (KNO_3). Both 1:1 and 2:1 chelates of unusually large stability were found. Trends in the formation constants are discussed and it is shown that the data can be explained by assuming that the hydroxyethyl group is coördinated in both the 1:1 and 2:1 chelates. The data also indicate that the rare earth ions have a coördination number larger than six in these species.

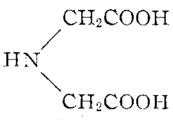
In connection with the project underway in this Laboratory in which the basic complexing tendencies of the rare earths are being investigated, the formation constants for the rare earth–N-hydroxyethyliminodiacetic acid (HIMDA) chelates have been measured and are reported herein. This ligand is of particular interest for several reasons. First of all, it has been rather extensively and carefully studied and the formation constants for a large number of HIMDA–metal chelates have been determined.[2,3] Comparison of these data with the corresponding formation constants for the rare earth chelates should be useful in obtaining information relative to the factors influencing the coördination of the rare earth ions.

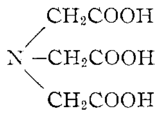
A second reason for investigating this ligand is the opportunity to compare these complexes with the corresponding complexes of iminodiacetic acid (IMDA).[4] Of primary interest here is the inductive effect of the N-hydroxyethyl group and the possibility of coördination through the hydroxy group. In addition, since HIMDA contains four potential donor sites, it is possible that in the 2:1 complexes the central rare earth ion has a coördination number larger than six.

The only previous studies with the rare earth complexes of HIMDA appear to be an investigation of some mixed complexes with N-hydroxyethylethylenediaminetriacetic acid,[5] a study of the hydrolysis of the lanthanum chelate,[6] and a study of the ligand as an eluent in the ion-exchange separation of the rare earths.[7]

The structural formulas of HIMDA and the other ligands which are mentioned in this paper are given below.


HIMDA


IMDA


NTA

Experimental

Solutions.—The HIMDA was obtained from the Dow Chemical Company and was purified by two recrystallizations from water. An approximately 0.005 *M* solution was prepared by dissolving the required amount of acid in de-ionized water and was standardized by potentiometric titration both in the presence and absence of copper(II) ions. The preparation and standardization of the 0.005 *M* rare earth nitrate[8] and 1.000 *M* potassium nitrate solutions have been described previously.[4] A solution 0.005 *M* in tren·3HCl (tren is 2,2′,2″-triaminotriethylamine) was prepared by dissolving the required amount in de-ionized water and was standardized by potentiometric titration in the presence of copper(II) nitrate. All other metal ion solutions were prepared from the analytical reagents and standardized complexometrically. For the measurements using the copper amalgam electrode a 0.05 *M* HIMDA solution was prepared so that the total ionic strength was 0.1 using potassium nitrate as the inert salt.

Copper(II) Amalgam.—The liquid copper amalgam, 2.00% by weight, was prepared by electrolyzing a solution of copper(II) sulfate with pure mercury as the cathode. The amalgam was stored under dilute nitric acid and an atmosphere of nitrogen.

Experimental Procedures.—(a) pH method: In those cases where the 1:1 complex was not too stable ($\log K_1 < 9$), the direct titration procedure described previously[4] was used with solutions containing HIMDA and the rare earth ion in the ratio 1:1, 2:1,

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[1] National Science Foundation Undergraduate Research Participant, 1961–1962.

[2] G. Schwarzenbach, G. Anderegg, W. Schneider, and H. Senn, *Helv. Chim. Acta*, **38**, 1147 (1955).

[3] S. Chaberek, Jr., R. C. Courtney, and A. E. Martell, *J. Am. Chem. Soc.*, **74**, 5057 (1952).

[4] L. C. Thompson, *Inorg. Chem.*, **1**, 490 (1962).

[5] L. C. Thompson and J. A. Loraas, *ibid.*, **2**, 89 (1963).

[6] R. C. Courtney, R. L. Gustafson, S. Chaberek, Jr., and A. E. Martell, *J. Am. Chem. Soc.*, **80**, 2121 (1958).

[7] L. Wolf and J. Massone, *J. Prakt. Chem.*, **5**, 288 (1958), and references therein.

[8] The rare earth materials were generously supplied by Lindsay Chemical Division, American Potash and Chemical Corporation, West Chicago, Illinois.

or 3:1. (b) tren method: The procedure consisted of a potentiometric titration of a 1:1:1:1 solution of the rare earth ion, copper(II), tren·3HCl, and HIMDA using the same apparatus and technique as in the direct titration procedure. (c) Copper(II) amalgam: The apparatus used in this procedure consisted of a 200-ml. Berzelius beaker and a stopper which contained holes for the glass and calomel electrodes, the nitrogen inlet tube, the copper amalgam electrode, and the buret. The calomel electrode was modified by coating the inside with a thin layer of agar prepared so that it was 0.1 *M* in potassium nitrate. The copper amalgam electrode consisted of a Sargent S-30438 Reilley electrode with the amalgam placed in the annular cup. The potentials of the amalgam–calomel assembly were read with a Leeds and Northrup type K-3 potentiometer. The cell is described by

$$\begin{array}{r|l||l||l|} \text{Cu, Hg} & \text{experimental solution} & 0.1\ M\ \text{KNO}_3 & \text{satd. KCl} \\ \text{glass} & \mu = 0.1\ (\text{KNO}_3) & & \end{array}$$
$$\text{Hg}_2\text{Cl}_2\text{, Hg } (25°)$$

The concentration of copper(II) in the solution was found from $E = E^{0\prime} + 0.02958 \log [\text{Cu}^{2+}]$. The value of $E^{0\prime}$ was determined in solutions where there was little reduction to copper(I) and was found to have the value 0.3348 v. Solutions containing a known concentration of copper(II) and rare earth ion in a medium of $\mu = 0.1$ (KNO_3) were titrated with the 0.05 *M* HIMDA solution at a constant pH of 3.20 (maintained by the addition of 0.1 *M* KOH). The potential of the cell was read after each addition of HIMDA and base.

Calculations.—(a) pH method: The acid dissociation constants were determined as outlined by Chaberek and Martell.[9] Since both 1:1 and 2:1 chelates were formed, the method of Block and McIntyre[10] was used to solve the sets of simultaneous equations. The lanthanum system also was solved using the computer program developed by Professor Z Z. Hugus, Jr.[11] The agreement between the two methods of computation was excellent. (b) tren method: The usual calculations[12] were carried out and values for the formation constants of some of the 1:1 chelates were obtained. (c) Copper amalgam method: This method has been discussed in detail previously[13] and only the relevant features are mentioned here. In the region in which $[\text{HIMDA}]_t > [\text{Cu}^{2+}]_t$ for solutions containing only copper(II) and HIMDA, eq. 1–3 hold and the copper–HIMDA formation constant is easily

$$[\text{Cu}^{2+}]_t = [\text{CuX}] \qquad \text{X} = \text{HIMDA}^{2-} \tag{1}$$

$$[\text{HIMDA}]_t = [\text{H}_2\text{X}] + [\text{HX}] + [\text{X}] + [\text{CuX}] \tag{2}$$

$$K_{\text{Cu/CuX}} = \frac{[\text{CuX}]}{[\text{Cu}^{2+}][\text{X}]} \tag{3}$$

calculated since the value of $[\text{Cu}^{2+}]$ was measured and the pH was maintained at a constant, known value.

In all the solutions, both those containing only copper(II) and those containing copper(II) and the rare earth ion, if $[\text{Cu}^{2+}]_t$ is kept constant, then the principle of corresponding solutions[14] asserts that solutions having the same potential for the copper amalgam electrode also have the same concentration of **X**. Since the rare earth ion is complexed by some of the HIMDA, this point of equal $[\text{Cu}^{2+}]$ is reached only when more HIMDA has been added to the second solution than to the first. Equations 4 and 5 result from this condition.

$$[\text{HIMDA}]_2 - [\text{HIMDA}]_1 = [\text{LnX}] \tag{4}$$

$$\bar{n} = \frac{[\text{LnX}]}{[\text{Ln}]_t} = \frac{[\text{HIMDA}]_2 - [\text{HIMDA}]_1}{[\text{Ln}]_t} \tag{5}$$

The free ligand concentration is found from the values of $[\text{Cu}^{2+}]$, $K_{\text{Cu/CuX}}$, and $[\text{CuX}]$. Since $[\text{Cu}^{2+}]$ is $<1\%$ of $[\text{Cu}]_t$ in the region which was used in the calculations, the last term was found from the relationship $[\text{CuX}] \cong [\text{Cu}]_t$. For the rare earth ions only $\bar{n}$ values less than one could be obtained by this method. In order to evaluate the formation constants, these values of $\bar{n}$ were combined with the $\bar{n}$ values greater than one obtained by the direct pH method.

Results

The results which were calculated for the acid dissociation constants and the rare earth–HIMDA formation constants are listed in Table I. Some comment is necessary concerning the experimental methods used in obtaining these values. The direct pH method can only be used to determine values of log *K* which are no larger than the p*k* value for the dissociation of the last proton from the ligand.[15] This means that the formation constant for the 1:1 rare earth–HIMDA complexes for the rare earths heavier than neodymium cannot be determined accurately by this method.

The usual way to circumvent this difficulty is to use the "tren" method.[12,15] This works quite well providing that the 1:1 and 2:1 chelates have formation constants which are different enough so that one or the other of the chelates may be neglected. If this is not the case, then although the method can still be used in principle, in actual practice the calculations are quite cumbersome and unwieldy and since they involve so many equilibrium constants, the values which are obtained are subject to rather large errors.

The copper amalgam electrode can be used to avoid both of these difficulties[13]; but since data can only be obtained for the region $\bar{n} < 1$, they must be combined with the data obtained by the pH method for the region $1 < \bar{n} < 2$ in order to calculate the formation constants.

TABLE I

FORMATION CONSTANTS FOR THE RARE EARTH–HIMDA CHELATES

$t = 25°$; $\mu = 0.1$ (KNO_3); $\text{p}k_1 = 1.91$; $\text{p}k_2 = 8.72$

Metal ion	log K_1[a]	log K_2[b]	Method for log K_1
La^{3+}	8.00 ± 0.01[c]	5.98 ± 0.01	Direct pH
Ce^{3+}	8.46 ± 0.03	6.56 ± 0.02	Direct pH
Pr^{3+}	8.64 ± 0.03	6.86 ± 0.02	Direct pH
Nd^{3+}	8.80 ± 0.02	7.13 ± 0.01	Direct pH
Sm^{3+}	9.10 ± 0.03	7.77 ± 0.02	tren
Eu^{3+}	9.10 ± 0.02	7.91 ± 0.02	Cu-electrode
Gd^{3+}	9.01 ± 0.03	8.04 ± 0.03	Cu-electrode
Tb^{3+}	9.08 ± 0.02	8.19 ± 0.02	Cu-electrode
Dy^{3+}	9.08 ± 0.02	8.30 ± 0.02	Cu-electrode
Ho^{3+}	9.18 ± 0.03	8.13 ± 0.02	Cu-electrode
Er^{3+}	9.24 ± 0.02	7.98 ± 0.01	Cu-electrode
Tm^{3+}	9.35 ± 0.03	7.88 ± 0.01	Cu-electrode
Yb^{3+}	9.38 ± 0.02	7.74 ± 0.02	Cu-electrode
Lu^{3+}	9.50 ± 0.02	8.02 ± 0.02	Cu-electrode
Y^{3+}	9.22 ± 0.01	7.61 ± 0.02	Cu-electrode

[a] $K_1 = [\text{LnX}]/[\text{Ln}][\text{X}]$. [b] $K_2 = [\text{LnX}_2]/[\text{LnX}][\text{X}]$. [c] 95% confidence limits based on maximum deviation from the average.

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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) Z Z. Hugus, Jr., in "Advances in the Chemistry of the Coördination Compounds," ed. by S. Kirschner, The Macmillan Company, New York, N. Y., 1961, p. 379. We are grateful to Professor Hugus for solving these data.

(12) H. Ackermann and G. Schwarzenbach, *Helv. Chim. Acta*, **32**, 1544 (1949).

(13) G. Anderegg, *ibid.*, **43**, 414 (1960).

(14) F. J. C. Rossotti and H. Rossotti, "The Determination of Stability Constants," McGraw-Hill Book Company, New York, N. Y., 1961, p. 152.

(15) G. Schwarzenbach and E. Freitag, *Helv. Chim. Acta*, **34**, 1492 (1951).

The experimental procedures and computational techniques that were used were checked by determining the formation constants of some HIMDA chelates for which values are recorded in the literature.[2,3] For the pH method these were the 1:1 formation constant of calcium (log K_1 = 4.74, t = 25°; literature values 4.63, t = 20°, and 4.83, t = 30°) and the 2:1 formation constant for copper (log K_2 = 4.11, t = 25°; literature values 4.01, t = 20°, and 4.23, t = 30°). Using the tren method, and the known value for the 1:1 lanthanum–HIMDA chelate, the formation constant for the 1:1 copper–HIMDA chelate was found to be 11.72 (literature 11.86, t = 20°). The copper amalgam method also gave 11.72 for the 1:1 copper–HIMDA chelate. It is seen that in all cases the agreement was excellent.

Moreover, whenever it was possible to calculate the value of the rare earth–HIMDA formation constants by more than one method, the agreement was quite satisfactory (*e.g.*, the value of log K_1 for neodymium determined using the tren method was 8.77 compared to 8.80 by the direct method; for europium the tren method gave 9.08 compared to 9.10 determined with the copper electrode).

Discussion

The values of pk_1 and pk_2 for HIMDA determined in this study are in good agreement with those in the literature (20°, pk_1 = 2.2 and pk_2 = 8.73[2]; 30°, pk_1 = 1.96, pk_2 = 8.78[3]).

The formation constants for the 1:1 rare earth–HIMDA chelates follow essentially the same pattern which was found for the IMDA chelates.[4] There is, however, a more pronounced discontinuity in the region of gadolinium (the so-called "gadolinium break") and yttrium has the "normal" position between holmium and erbium.[16] It is of interest to note that the spread in log K_1 values in the light rare earths from lanthanum to europium is 1.10 log K units, whereas in the heavy rare earths the spread from terbium to lutetium is only 0.42 log K unit. The corresponding values for the IMDA chelates are 0.85 and 0.83 log K unit, respectively. This would seem to indicate that the two chelating agents have slightly different chelating characteristics particularly with the heavier rare earth ions and might be indicative of a slight steric effect in the HIMDA chelates of the smaller ions.

If HIMDA behaves as a terdentate ligand utilizing only the same donor atoms as IMDA, it would be expected that the chelates which it forms would be weaker than those of IMDA due to the decreased basicity of the nitrogen atom. However, it has been noted previously[2,3] that in all cases the 1:1 HIMDA chelate is more stable than the corresponding 1:1 IMDA chelate by about 1.3 log K units. This has been interpreted to mean that the hydroxyl group is coördinated to the metal ion in question.

Comparison of the formation constants for the rare earth–HIMDA chelates with those for the IMDA chelates shows that the HIMDA chelates are the more stable by 1.9 log K units in the case of lutetium and 2.5 log K units in the case of samarium. This would indicate that the hydroxyl group of HIMDA is coördinated to the rare earth ions. The fact that the difference in the log K values of the HIMDA and IMDA chelates is larger for the rare earths than for the other metals that have been investigated reflects the facts that the rare earths coördinate more readily to oxygen donors and that they are trivalent, whereas the other metals are divalent.

The formation constants for the 2:1 HIMDA–rare earth chelates increase steadily from lanthanum to dysprosium and then decrease to ytterbium. The increase at lutetium is similar to that noted for the 2:1 nitrilotriacetic acid (NTA)–rare earth chelate[17] and at present is unexplained. The maximum at dysprosium is indicative of increasing steric hindrance to the attachment of the second ligand. The location of yttrium, with respect to the formation constant of its 2:1 chelate, between neodymium and samarium would classify it as "abnormal."[16]

The most interesting feature in the formation constants of the 2:1 chelates is their magnitude both in an absolute sense and relative to the 1:1 chelates. In all cases the value of K_1/K_2 is $\leq 10^2$ for the HIMDA–rare earth chelates. In addition, the 2:1 chelates are considerably more stable than the 2:1 IMDA chelates (1.89 log K units for ytterbium to 2.87 log K units for dysprosium). Both of these facts support the assumption that the hydroxyl group of the second HIMDA molecule also is coördinated in the 2:1 complex.

This behavior with the rare earth ions is quite different from that of any of the other ions which have been studied previously. Data have been obtained only for the copper, nickel, cobalt, and zinc chelates of both HIMDA and IMDA and a comparison of the 2:1 HIMDA chelates of these metals[2,3] with their IMDA analogs[9] shows that for each of the metals the 2:1 HIMDA chelate is *less* stable by 0.9–1.4 log K units. This is the behavior which is expected since each of these metal ions has a maximum coördination number of six. The addition of the second ligand to the 1:1 complex in these cases would displace the hydroxyl group and the resulting chelate would utilize the same arrangement of donor atoms as in the IMDA chelate. The decreased basicity of the nitrogen atom then would contribute to the decrease in the log K_2 value of the HIMDA chelate as compared with the log K_2 value of the IMDA chelate.

The magnitude of this difference for the rare earth ions can be explained most readily by assuming that the coördination number in these species is greater than six; presumably eight. In several previous cases for which the ligands had an excess of donor atoms over that required for six-coördination, it also has been

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(16) T. Moeller, L. C. Thompson, and R. Ferrús, in "Rare Earth Research," ed. by E. V. Kleber, The Macmillan Company, New York, N. Y., 1961, p. 3.

(17) T. Moeller and R. Ferrús, *Inorg. Chem.*, **1**, 49 (1962).

necessary to invoke this same assumption.[18] A definitive answer to this question must, of course, await a detailed structural determination of one of these complexes.

Acknowledgment.—This investigation was supported in part by PHS Research Grant GM-08394 from the Division of General Medical Studies, Public Health Service, and in part by the National Science Foundation through its Undergraduate Research Participation Program.

[18] Reference 5 and papers cited therein.

CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY AND
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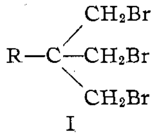
Sexadentate Chelate Compounds. XI

BY ROWLAND W. GREEN, KENNETH W. CATCHPOLE, ARPAD T. PHILLIP,[1] AND FRANCIS LIONS

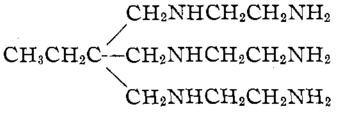
Received February 23, 1963

The base 5-ethyl-5-(δ-amino-β-azabutyl)-1,9-diamino-3,7-diazanonane has been synthesized and shown to be capable of functioning as a sexadentate chelating agent. Some sexadentate chelate compounds containing it have been prepared and stability constants of certain of its complexes determined. Its ability to function sometimes as a quadridentate chelating agent enables it to be used in the synthesis of certain multi-nucleate ammines whose cations carry high positive charges.

Heating together of 1-bromo-2,2-bis-(bromomethyl)-butane (I; R = C_2H_5) and ethylenediamine in large excess under reflux for some considerable time yields a mixture of bases from which 5-ethyl-5-(δ-amino-β-azabutyl)-1,9-diamino-3,7-diazanonane (II) can be isolated in reasonable yield. Similar type reactions between poly-bromo compounds and ethylenediamine have been extensively studied previously by van Alphen and co-workers.[2] Hexamines homologous to II should similarly be accessible from available 1,1,1-trimethylolalkanes.


$R{-}C(CH_2Br)_3$

I


$CH_3CH_2C(CH_2NHCH_2CH_2NH_2)_3$

II

Models show that it is readily possible for the molecules of the base II so to arrange themselves spatially that all six nitrogen atoms can be simultaneously presented and bonded to a six-coördinate metal atom of suitable size from the apices of a circumscribing octahedron in one or the other of two enantiomorphous arrangements (Fig. 1). Thus, II should be capable of functioning as a sexadentate chelating agent of Type 9 of the classification previously suggested by one of us.[3] Sexadentates with this donor atom pattern have been previously described.[4] The only recorded saturated aliphatic hexamine previously demonstrated to be capable of functioning as a sexadentate chelating agent would appear to be the base "penten," (III) which is of Type 4[3] and which was prepared and studied by Schwarzenbach and co-workers.[5] The base II resembles III in that both bases present six aliphatic nitrogen donor atoms to a metal atom when coördinating as sexadentate chelating agents. However, in II three of these are primary and three secondary amino, while in III four are primary and two tertiary amino nitrogen atoms.

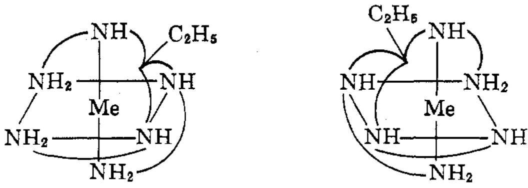
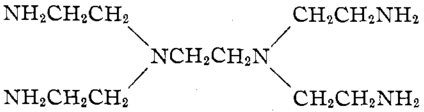


Figure 1.


$(NH_2CH_2CH_2)_2NCH_2CH_2N(CH_2CH_2NH_2)_2$

III

II coördinates readily with nickel(II) salts and a pink crystalline iodide, $Ni(C_{12}H_{32}N_6)I_2$, can be isolated whose magnetic moment (3.1 B.M. at 20°) is consistent with its formulation as a sexadentate chelate compound. II also appears to coördinate as a simple sexadentate with cobalt(III) salts since the gold-colored diamagnetic salt $Co(C_{12}H_{32}N_6)Cl_3 \cdot H_2O$ was isolated from the brown solution obtained when sodium triscarbonatocobaltate-(III)-3-water[6] was stirred into a warm acid solution of II. Attempts to resolve this salt into its diastereoisomers have not so far succeeded.

On the other hand, from a solution of II and cobalt-(II) chloride in dilute hydrochloric acid that had been

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[1] Commonwealth Research Scholar, University of Sydney.

[2] J. van Alphen, *Rec. trav. chim.*, **55**, 412, 669, 835 (1936); **56**, 343, 529, 1007 (1937); **57**, 265 (1938).

[3] F. Lions, *Record Chem. Progr.*, **22**, 73 (1961).

[4] *Cf.*, *e.g.*, F. P. Dwyer, N. S. Gill, E. C. Gyarfas, and F. Lions, *J. Am. Chem. Soc.*, **79**, 1269 (1957).

[5] G. Schwarzenbach and P. Moser, *Helv. Chim. Acta*, **36**, 581 (1953), and subsequent papers.

[6] H. F. Bauer and W. C. Drinkard, *J. Am. Chem. Soc.*, **82**, 5031 (1960).