any other position. In **2** no such double-weighted structures can be written. Lastly, in **3**, **4**, and **7** the proton adjacent to the carbon bonded to the imino group shows very small contact shifts. This effect was encountered in the salicylaldimine complexes when theoretical and experimental spin densities were compared.[1] We are unable to explain this effect.

The proton resonance spectra of naphthalene and substituted naphthalenes are in general quite complex because the chemical shift differences δ_{ij} between two protons are of the same magnitude as the nuclear spin-spin coupling constants J_{ij}. Due to the spectral complexity the coupling constants are not readily obtainable. As Fig. 2 clearly shows, the presence of a small amount of spin density on the ligand reduces the spectra to first-order simplicity. Utilizing measurements of **1** and **2** such that $\delta_{ij}/J_{ij} > 10$ the coupling constants can be determined directly from the spectra. We have determined the following coupling constants (± 0.2 c.p.s.) in the 2-hydroxy-1-naphthaldimines: $J_{34} = 9.0$, $J_{56} = 7.9$, $J_{67} = 6.8$, and $J_{78} = 8.3$ c.p.s. From a study of the free ligand J_{34} has been found to be 9.1 ± 0.2 c.p.s. The remaining results compare very favorably with those obtained for the β-naphthyl group by a similar procedure[21]: $J_{56} = 8.2$, $J_{67} = 6.5$, $J_{78} = 8.1 \pm 0.2$ c.p.s. Both sets of values are in close agreement with the J_{ij} determined from the most recent analysis of the naphthalene spectrum.[27] If the correlation[21] between bond length and *cis* spin-spin coupling constants is meaningful, the C_3–C_4 bond should be ~0.01 Å. shorter than the C_5–C_6 and C_7–C_8 bonds and ~0.02 Å. shorter than the C_6–C_7 bond in **1**.

Acknowledgment.—Financial support from the National Science Foundation and the Milton Fund of Harvard University is gratefully acknowledged. Thanks are due Dr. B. D. Nageswara Rao for obtaining several of the spectra and Dr. G. O. Dudek for several helpful discussions.

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Complexes of the Rare Earths. VII. 2-Picolyliminodiacetic Acid and 6-Methyl-2-picolyliminodiacetic Acid[1]

BY LARRY C. THOMPSON

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The solution stabilities of the rare earth chelates of 2-picolyliminodiacetic and 6-methyl-2-picolyliminodiacetic acids have been measured at 25° and $\mu = 0.1$ (KNO_3). The former ligand apparently functions as a quadridentate ligand in both the 1:1 and 2:1 complexes, whereas the 6-methyl group apparently hinders the coordination of the pyridine nitrogen in the second ligand. The affinity of the rare earth ion for the heterocyclic nitrogen atom appears to be approximately the same as for the hydroxyl group in the analogous compound N-hydroxyethyliminodiacetic acid.

It has been observed quite generally that the rare earth ions form complexes predominantly with molecules which utilize oxygen as the donor atom.[2] In fact, the solution stabilities of rare earth complexes of organic ligands have been measured only for those ligands in which at least one oxygen atom acts as a donor atom.[3] Although this is the case, most workers are of the opinion that in molecules such as the aminopolycarboxylic acids in which the geometry requires the close proximity of the aliphatic nitrogen atoms to the rare earth ion, there is some interaction between the nitrogen atom and the rare earth. In a recent publication Grenthe and Fernelius[4] suggest that such may not be the case and, furthermore, that the heterocyclic nitrogen atom in the rare earth complexes of dipicolinic acid is consequently not coordinated. This then leads to the conclusion that in the 3:1 dipicolinic acid–rare earth chelates the coordination number is six.

Our earlier studies have led us to believe that the coordinating tendencies of the rare earths are somewhat broader than have been thought previously and we considered it worthwhile to investigate this problem in more detail. In particular, it was of interest to study the interaction between the pyridine ring and the rare earth ions.

In order to carry out this objective it was necessary to synthesize a compound in which the pyridine ring is suitably located so that the nitrogen atom could reasonably be expected to bond to the metal ion. The recent publication by Irving and da Silva[5] prompted us to use the iminodiacetate residue as the basic chelating structure and we report herein on the solution stabilities of the rare earth complexes of 2-picolyl-

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[1] Part VI: L. C. Thompson and J. A. Loraas, *Inorg. Chem.*, **2**, 594 (1963).

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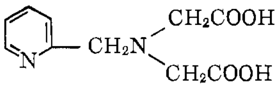
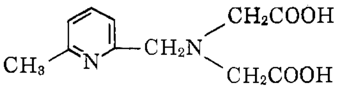
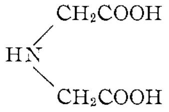
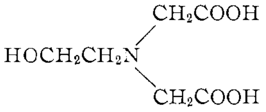
iminodiacetic acid. In addition, since it has been suggested previously[6-8] that nonchelating substituents in the 6-position can sterically hinder complex formation, we have prepared and studied 6-methyl-2-picolyliminodiacetic acid.

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


2-Picolyliminodiacetic acid


6-Methyl-2-picolyliminodiacetic acid


Iminodiacetic acid (IMDA)


N-Hydroxyethyliminodiacetic acid (HIMDA)

Experimental

Preparation of Ligands. (1) **2-Picolyliminodiacetic Acid.**—The ligand was prepared as previously described[5] with the exception that 2-picolylamine (Aldrich Chemical Co.) was used as a starting material. In contrast to the report in the literature, if the alkaline reaction mixture was made acidic by adding 6 *M* hydrochloric acid dropwise, the desired product separated when the pH reached a value of about 2.5. The ligand was separated from a small amount of sodium chloride by taking up in ethanol to which only the minimum amount of water was added to dissolve the entire material. When recrystallized from ethanol, the ligand had m.p. 184–185° (lit.[5] 174–175°). *Anal.* Calcd. for $C_{10}H_{12}N_2O_4$: C, 53.6; H, 5.4; N, 12.5. Found: C, 53.6; H, 5.5; N, 12.5.

(2) **6-Methyl-2-picolyliminodiacetic Acid.**—The ligand was prepared as above, substituting 2-aminomethyl-6-methylpyridine (Aldrich Chemical Co.). A slight excess of barium chloride was added to the alkaline reaction mixture and the precipitate of the barium salt of the ligand filtered. The barium content was determined as barium sulfate and then the stoichiometric quantity of 6 *M* sulfuric acid was added. After the $BaSO_4$ was filtered, the solution was concentrated, and precipitation of the desired acid was accomplished by scratching vigorously the walls of the beaker with a stirring rod. The resulting compound was recrystallized from aqueous alcohol and had m.p. 160–161°. *Anal.* Calcd. for $C_{11}H_{14}N_2O_4$: C, 55.5; H, 5.9; N, 11.8. Found: C, 54.7; H, 5.8; N, 12.1.

Although the error in the carbon analysis for this compound is rather large, the empirical formula calculated from these values agrees satisfactorily with that given. It should be pointed out that considerable difficulty was encountered in the analysis of both of these compounds with respect to obtaining analytical precision.

Solutions.—The solutions were prepared and standardized as described previously.[1,9,10]

Experimental Procedure.—The direct pH method and the tren method previously described[1] were used to determine the stability constants of the 2-picolyliminodiacetic acid complexes. The stability constants of the 6-methyl-2-picolyliminodiacetic acid were determined by the direct pH method.

Calculations. (1) **pH Method.**—The acid dissociation constants were determined as outlined by Chaberek and Martell.[11] Since both 1:1 and 2:1 chelates were formed, the method of Block and McIntyre was used to solve the sets of simultaneous equations.[12]

(2) **tren Method.**—Since the formation constants of the 2:1 chelates with 2-picolyliminodiacetic acid indicated that even in solutions containing the metal and ligand in a 1:1 ratio there would be some 2:1 chelate, the following equations hold under these experimental conditions (charges on the ions are omitted except where needed for clarity).

$$[\mathrm{Cu}]_t = C = [\mathrm{CuX}] + \epsilon[\mathrm{Cutren}] \qquad (1)$$

$$[\mathrm{Ln}]_t = C = [\mathrm{Ln}] + [\mathrm{LnX}] + [\mathrm{LnX_2}] \qquad (2)$$

$$[\mathrm{H_2X}]_t = C = [\mathrm{CuX}] + [\mathrm{LnX}] + 2[\mathrm{LnX_2}] \qquad (3)$$

$$[\mathrm{tren}]_t = C = [\mathrm{Cutren}] + \gamma[\mathrm{H_3tren}] \qquad (4)$$

$$[\mathrm{H}]_t = (3 - a)C = [\mathrm{H}] - [\mathrm{OH}] + \delta[\mathrm{H_3tren}] \qquad (5)$$

The coefficients ϵ, γ, and δ have their usual meanings[13] and a is the number of moles of base added per mole of tren. Equation 5 can be solved for [H$_3$tren], thus allowing eq. 4 to be solved for [Cutren] and eq. 1 for [CuX]. Equation 3 is then solved for [LnX] + 2[LnX$_2$]. This term combined with eq. 2 then yields $\bar{n}$.

$$\bar{n} = \frac{[\mathrm{LnX}] + 2[\mathrm{LnX_2}]}{[\mathrm{Ln}] + [\mathrm{LnX}] + [\mathrm{LnX_2}]} = \frac{(C - \gamma[\mathrm{H_3tren}])\epsilon}{C} \qquad (6)$$

The value of the concentration of the free ligand anion corresponding to each value of $\bar{n}$ is then obtained as follows.

$$\bar{K} = \frac{[\mathrm{H_3tren}]}{[\mathrm{H}]^3[\mathrm{tren}]} = \frac{[\mathrm{H_3tren}]}{(10^{-\mathrm{pH}})^3[\mathrm{tren}]} \qquad (7)$$

$$[\mathrm{Cu}] = \frac{[\mathrm{Cutren}]}{[\mathrm{tren}]K_{\mathrm{Cutren}}} = \frac{\{C - \gamma[\mathrm{H_3tren}]\}\bar{K}(10^{-\mathrm{pH}})^3}{K_{\mathrm{Cutren}}[\mathrm{H_3tren}]} \qquad (8)$$

$$[\mathrm{X}] = \frac{[\mathrm{CuX}]}{[\mathrm{Cu}]K_{\mathrm{CuX}}} = \frac{\{C - \epsilon(C - \gamma[\mathrm{H_3tren}])\}[\mathrm{H_3tren}]K_{\mathrm{Cutren}}}{K_{\mathrm{CuX}}\{C - \gamma[\mathrm{H_3tren}]\}\bar{K}(10^{-\mathrm{pH}})^3} \qquad (9)$$

Since K_{Cutren} and $\bar{K}$ are available from the literature and K_{CuX} can be obtained independently, pairs of $\bar{n}$ and [X] can be calculated and used in conjunction with the data from solutions containing the rare earth and ligand in the ratio of 1:2 (no tren or copper present). The formation constants can be obtained by solving the sets of simultaneous equations as above.

Results

The results which were obtained for the acid dissociation constants and the formation constants for the rare earth complexes of the ligands are given in Table I. Since the value of log K_1 for most of the rare earth chelates with 2-picolyliminodiacetic acid is greater than pk_2 of the ligand, the usual direct pH method is unsatisfactory.[14] If the tren method is used to circumvent this difficulty, it is found that in most cases the calculated values of log K_1 drift systematically to higher values. This is a consequence of the small difference between the formation constants of the 1:1 and 2:1 complexes. If the data from the titrations involving tren are used to compute $\bar{n}$ ([X]) pairs and these are combined with the data obtained from the direct 2:1 (ligand to metal) titrations, it is found that consistent values are obtained. Since several auxiliary formation constants are involved, the errors associated with this method of computation should be somewhat larger than those in the more direct methods, however.

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(6) H. R. Weimer and W. C. Fernelius, *J. Phys. Chem.*, **64**, 1951 (1960).

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TABLE I

FORMATION CONSTANTS[a] FOR THE RARE EARTH–2-PICOLYLIMINODIACETIC ACID CHELATES AND THE RARE EARTH–6-METHYL-2-PICOLYLIMINODIACETIC ACID CHELATES AT 25°, μ = 25°

Metal ion	2-Picolyliminodiacetic acid $pk_1 = 2.6$; $pk_2 = 8.21$		6-Methyl-2-picolyliminodiacetic acid $pk_1 = 3.46$; $pk_2 = 8.30$	
	log K_1	log K_2	log K_1	log K_2
La^{3+}	7.80	5.90	5.72	3.85
Ce^{3+}	8.30	6.44	6.00	4.07
Pr^{3+}	8.53	6.95	6.18	4.24
Nd^{3+}	8.64	7.18	6.28	4.26
Sm^{3+}	8.92	7.96	6.57	4.48
Eu^{3+}	8.92	8.02	6.76	4.50
Gd^{3+}	8.76	8.01	6.71	4.61
Tb^{3+}	8.87	8.17	7.16	4.94
Dy^{3+}	9.00	8.03	7.23	4.92
Ho^{3+}	9.07	7.80	7.30	5.03
Er^{3+}	9.25	7.65	7.42	5.22
Tm^{3+}	9.40	7.61	7.54	5.27
Yb^{3+}	9.60	7.73	7.65	5.33
Lu^{3+}	9.72	7.75	7.60	5.39
Y^{3+}	8.63	7.38	6.84	4.74

[a] These are the averages of at least six individual values and in no case is the maximum deviation of a single value greater than ±0.05 from the average.

The values of the acid dissociation constants of 2-picolyliminodiacetic acid are in satisfactory agreement with the values in the literature[5] ($pk_1 = 2.85$, $pk_2 = 8.25$, $\mu = 0.1$, at 20°). The experimental procedure and computational technique were checked by determining the formation constants of the 1:1 chelates with calcium and manganese. The values obtained ($\log K_1 = 4.89$ for calcium and $\log K_1 = 7.14$ for manganese, $\mu = 0.1$, at 25°) are in satisfactory agreement with the literature values[5] ($\log K_1 = 4.92$ for calcium and $\log K_1 = 6.97$ for manganese, $\mu = 0.1$, at 20°).

The tren method requires a value for the formation constant of the 1:1 copper complex. This was obtained by using both calcium and manganese as the auxiliary metal ion in the tren method. The agreement between the two calculations was good ($\log K_{CuX} = 14.02$ using calcium and $\log K_{CuX} = 14.11$ using manganese). The average value $\log K_{CuX} = 14.07$ was used in subsequent calculations. A further check on the methods used is obtained from the lanthanum system which could be studied using both the direct pH and tren methods. The direct pH method yields $\log K_{1_{LaX}} = 7.83$ and the tren method yields $\log K_{1_{LaX}} = 7.80$.

In calculating the formation constants of the 2:1 rare earth–6-methyl-2-picolyliminodiacetic acid chelates, it was apparent that at the higher pH values hydrolysis was beginning to interfere. Consequently, only values of $\bar{n} \leq 1.5$ were used to calculate the values of $\log K_2$. Since this is apparently the first study of the formation constants of this ligand, it was not possible to check any previous values.

Discussion

The over-all trend in the formation constants of the rare earth–2-picolyliminodiacetic acid chelates is remarkably similar to that of the rare earth–N-hydroxyethyliminodiacetic acid (HIMDA) chelates.[1] The values of $\log K_1$ increase to samarium and then there is a decrease to gadolinium, resulting in the so-called "gadolinium break." From gadolinium through lutetium the formation constants increase. The only major difference between the formation constants for the rare earth chelates with the ligands HIMDA and 2-picolyliminodiacetic acid lies in the position of the yttrium chelate. Whereas yttrium would be classed as "normal" in the HIMDA series, in the 2-picolyliminodiacetic acid series it appears in the cerium earth region between praseodymium and neodymium.

The conclusion that 2-picolyliminodiacetic acid functions as a quadridentate ligand toward the rare earth ions is reached due to the fact that even though the ligand is less basic than IMDA, it forms chelates which in all cases are about 2 log K units more stable.[9] A similar conclusion has also been reached in the case of a series of divalent metal ions.[5] This enhancement in stability is considered in more detail below.

Of particular interest are the magnitudes of the formation constants of the 2:1 chelates. These values are larger than for the IMDA chelates by 1.6 log K_2 units for ytterbium to 2.7 log K_2 units for terbium although the ligand is less basic. Since the 2:1 chelates of 2-picolyliminodiacetic acid with other metal ions are generally less stable[5] than the corresponding 2:1 IMDA chelates,[11] it would appear that the ligand is again functioning as a quadridentate toward the rare earths and that the coordination number of the rare earth is therefore larger than six. A discussion of this point has been given previously.[1,15]

Additional confirmation for the conclusion that the pyridine nitrogen atom is coordinated in 2-picolyliminodiacetic acid chelates is obtained by considering the 6-methyl-2-picolyliminodiacetic acid chelates. Although the two ligands have very similar values of pk_2, the values for the 1:1 rare earth–2-picolyliminodiacetic acid chelates are in all cases at least 1.7 log K units larger than those for the 6-methyl-2-picolyliminodiacetic acid chelates, which have formation constants of approximately the same magnitude as the IMDA chelates. Because of the decreased basicity in these ligands as compared to IMDA, this would indicate that in both cases the pyridine nucleus is participating in complex formation but that in the 6-methyl derivative the methyl group sterically hinders complexation of the pyridine ring. Similar conclusions have been reached for metals other than the rare earths with other pairs of ligands such as picolinic and 6-methylpicolinic acids[7] and 2-picolylamine and 6-methyl-2-picolylamine.[6]

In the 2:1 complexes in which the steric effect should be even more marked, 6-methyl-2-picolyliminodiacetic acid forms complexes with the rare earths which are of lower stability than the corresponding IMDA chelates. This implies that in these chelates the methyl group more effectively hinders the approach of the pyridine nitrogen atom to the rare earth ion.

(15) L. C. Thompson, *J. Inorg. Nucl. Chem.*, **24**, 1083 (1962).

The fact that the rare earth complexes of 2-picolyliminodiacetic acid are nearly as stable as the HIMDA chelates despite the decreased basicity of the ligand is very interesting. A semiquantitative estimate of this enhancement of stability could be obtained if there were a relationship between the log K_1 values of rare earth chelates and the pK values of the ligands. Although such a relationship is not available at present, it can still be concluded that the pyridine ring in this chemical environment is at least as effective in coordinating to the rare earths as the hydroxyl group of HIMDA, and in view of the basicity difference, probably slightly more so.

From this conclusion it is quite reasonable to expect that in the rare earth–dipicolinic acid chelates mentioned at the beginning of this paper, in which the pyridine ring is sterically required to be juxtaposed to the metal ion, there is an interaction (bonding) between the heterocyclic nitrogen atom and the rare earth ion. That this is not an isolated example is shown by the fact that picolinic acid itself forms rather strong chelates with rare earth ions.[16] The stability of the rare earth complexes of 8-hydroxyquinoline and its derivatives[17] should also be recalled.

An explanation for this effect is not forthcoming, since the factor which should stabilize pyridine complexes, suitably oriented d-orbitals for π-bonding, is missing in these ions. It has recently been shown that the alkaline earths behave in much the same way and no explanation could be offered.[5] For both of these groups of metals, however, the effect of the pyridine ring is much less than for the other metals which have been studied. This is probably due to the fact that the alkaline earths and rare earths are bonded to the pyridine ring using only the σ-bonding character. Since the structure of the ligand is such that the nitrogen atom of the pyridine ring can approach a bonding position which is occupied by a water molecule, it is possible that the combination of the larger dipole moment of pyridine, compared with that of water, and the extra stability conferred on the structure by the additional chelated group are sufficiently large to displace the coordinated water molecule. Whatever the explanation, it is apparent that the rare earths coordinate to the pyridine ring in suitable environments more readily than had been expected.

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Chloro Complexes of Nitrosylruthenium[1a]

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Received July 17, 1963

An investigation of the nitrosylruthenium chloro complexes formed in hydrochloric acid solutions has shown the existence of five monomeric complexes. The mono-, di-, tri-, tetra-, and pentachloro complexes were isolated by ion exchange and were shown to have the formulas $RuNOCl(H_2O)_4^{+2}$, $RuNOCl_2(H_2O)_3^+$, $RuNOCl_3(H_2O)_2$, $RuNOCl_4(H_2O)^-$, and $RuNOCl_5^{-2}$ in acid media. The complex $RuNOCl_4(H_2O)^-$ is a weak acid that dissociates to produce $RuNOCl_4(OH)^{-2}$ with a dissociation constant of 9.5×10^{-7}. $RuNOCl_3(H_2O)_2$ is a weak dibasic acid that dissociates to produce $RuNOCl_3(H_2O)(OH)^-$ and $RuNOCl_3(OH)_2^{-2}$ with successive dissociation constants of 1.1×10^{-5} and 3.4×10^{-8}. One other chloro complex was detected but was not characterized.

Introduction

Solid crystalline chloro compounds of nitrosylruthenium such as $RuNOCl_3 \cdot 5H_2O$ and $K_2RuNOCl_5$ have been known for years. More recently amorphous $H_2RuNOCl_4OH \cdot 2H_2O$ and crystalline $(NH_4)_2[RuNOCl_4OH]$ have been studied,[2] but no chloro nitrosylruthenium complexes have been identified in solution. A study of the hydrolysis of $RuNOCl_3(H_2O)_2 \cdot 3H_2O$ by Thomas and Mucci[3] was interpreted as supporting only $RuNO(H_2O)_5^{+3}$ and $RuNO(H_2O)_4(OH)^{+2}$ in solution.

The present investigation deals with the isolation from aqueous solutions and characterization of chloro complexes of nitrosylruthenium. $[RuNOCl_5]^{-2}$, $[RuNOCl_4H_2O]^-$, $RuNOCl_3(H_2O)_2$, $[RuNOCl_2(H_2O)_3]^+$, and $[RuNOCl(H_2O)_4]^{+2}$ present in mixtures of aqueous hydrochloric acid and $RuNOCl_3(H_2O)_2 \cdot 3H_2O$ were separated by ion-exchange resins and their formulas were established.

Experimental

Preparation of Solid Compounds. $RuNOCl_3(H_2O)_2 \cdot 3H_2O$.—A mixture of chloro complexes of nitrosylruthenium was prepared by dissolving nitrosylruthenium hydroxide, prepared by the

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[1] (a) The information contained in this article was developed during the course of work under contract AT(07-2)-1 with the U. S. Atomic Energy Comission; (b) inquiries relating to this paper should be directed to this author.

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