Complexes of the Rare Earths. VIII.[1] Picolinic Acid

BY LARRY C. THOMPSON

The solution stabilities of the complexes between picolinic acid and the rare earths have been measured at 25° and ionic strength 0.1 M (KNO$_3$). The complexes are somewhat stronger than might have been expected. Evidence is presented from which it is concluded that the heterocyclic nitrogen atom is coordinated as well as the carboxyl group.

Although there has been renewed interest in the coordination chemistry of the rare earths with simple ligands, nearly all the work on formation constants of rare earth complexes has been concerned with the affinity of various oxygen donors. Recently, however, several groups have been studying the sulfur atom in the mercapto group[2-6] and the nitrogen atom in the amino group[2] as potential donors to the rare earth ions. It has proved to be quite difficult to get an accurate estimate of the donor properties of these groups toward the rare earths. In the case of the mercapto group, the problem has been that the only compounds which have been studied are of such low stability that it is difficult to obtain reliable figures. The amino group presents a different problem in that it is generally present in the ammonium form at pH values at which hydrolysis of the rare earth ion can be neglected.

As part of a study designed to expand the information on the coordination chemistry of the rare earths, the pyridine nucleus was studied recently as a donor toward rare earth ions by incorporating it into the iminodiacetic acid structure.[1] The results of this study suggested that it would be interesting to investigate a much simpler molecule in which the pyridine nucleus would be expected to be bonded to the rare earths. Picolinic acid was chosen for such a study and the solu-

picolinic acid
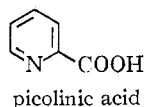
tion stabilities of its rare earth complexes are reported in this communication.

The reasons for choosing picolinic acid were threefold. (1) The solution stabilities of many of its complexes have been studied previously.[7] (2) It is analogous to glycolic acid, mercaptoacetic acid, and glycine and it should be possible to assess at least part of the difference in stability of complexes of these ligands to be the difference in donor ability of the pyridyl and hydroxyl, mercapto, and amino groups. (3) The nitrogen atom

is only weakly basic toward the proton and there is no experimental difficulty due to the hydrolysis of the rare earth ions.
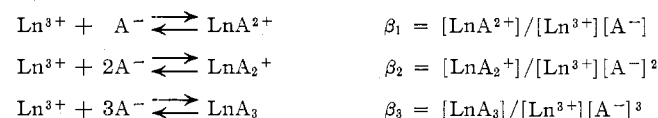
Experimental

Solutions.—The picolinic acid was purchased from Aldrich Chemical Company and purified by two recrystallizations from water. An approximately 0.05 M solution was prepared by dissolving the required amount of acid in de-ionized water and was standardized by potentiometric titration. The remaining solutions were prepared as described previously.[8,9] For the experimental measurements solutions were prepared in which the ratio of ligand to metal was either 1:1 or 10:1. (The approximate concentration of the picolinic acid was either 0.001 or 0.01 M.) The ionic strength was made 0.10 by the addition of potassium nitrate and at the end of the titration was always less than 0.12.

Experimental Procedure.—The experimental procedure consisted of a potentiometric titration of the 1:1 and 10:1 solutions as described previously.[8] The only difference was that the pH meter was operated as a Model GS and pH values were recorded to ±0.0025 pH unit. The pH scale was calibrated between pH 3 and 4 by measuring the pH of solutions of nitric acid having $\mu = 0.10$ M (KNO$_3$). The correction factor which was found (-0.067 ± 0.002 pH unit) was used in all subsequent measurements. The pH meter was standardized before and after each titration with the same Beckman pH 4 buffer solution. One buffer solution was used throughout the entire study.

Calculations.—Preliminary values of the formation constants were obtained by using the graphical method proposed by Rossotti and Rossotti.[10] These preliminary values were then used as input data in the computer program, GAUSS G, developed by Tobias,[11] and the formation constants refined by this program are the ones reported in this paper. For each metal ion 30–40 experimental points from both the 1:1 and 10:1 solutions were considered.

Results

The values of the acid dissociation constant of picolinic acid and the formation constants of the rare earth–picolinic acid complexes are given in Table I. The β-values are the equilibrium constants for the reactions

$$Ln^{3+} + A^- \rightleftarrows LnA^{2+} \qquad \beta_1 = [LnA^{2+}]/[Ln^{3+}][A^-]$$

$$Ln^{3+} + 2A^- \rightleftarrows LnA_2^+ \qquad \beta_2 = [LnA_2^+]/[Ln^{3+}][A^-]^2$$

$$Ln^{3+} + 3A^- \rightleftarrows LnA_3 \qquad \beta_3 = [LnA_3]/[Ln^{3+}][A^-]^3$$

(1) Part VII: L. C. Thompson, *Inorg. Chem.*, **3**, 1015 (1964).

(2) M. Cefola, A. S. Tompa, A. V. Celiano, and P. S. Gentile, *ibid.*, **1**, 290 (1962).

(3) J. L. Bear, G. R. Choppin, and J. V. Quagliano, *J. Inorg. Nucl. Chem.*, **24**, 1601 (1962).

(4) J. L. Bear, G. R. Choppin, and J. V. Quagliano, *ibid.*, **25**, 513 (1963).

(5) I. Grenthe, *Acta Chem. Scand.*, **16**, 1695 (1962).

(6) R. S. Kolat, Ph.D. Dissertation, Iowa State University of Science and Technology, 1961.

(7) G. Anderegg, *Helv. Chim. Acta*, **43**, 414 (1960), and references therein.

(8) L. C. Thompson, *Inorg. Chem.*, **1**, 490 (1962).

(9) The rare earth materials were generously supplied by Lindsay Chemical Division, American Potash and Chemical Corporation, West Chicago, Ill.

(10) F. J. C. Rossotti and H. S. Rossotti, *Acta Chem. Scand.*, **9**, 1166 (1955).

(11) R. S. Tobias and M. Yasuda, *Inorg. Chem.*, **2**, 1307 (1963).

TABLE I

FORMATION CONSTANTS FOR THE RARE EARTH–
PICOLINIC ACID COMPLEXES

$t = 25°$; $\mu = 0.1\ M\ (KNO_3)$; $pK = 5.204$

Metal ion	log $\beta_1{}^a$	log $\beta_2{}^a$	log $\beta_3{}^a$
La^{3+}	3.54	6.28	8.9
Ce^{3+}	3.74	6.56	9.5
Pr^{3+}	3.85	6.96	9.9
Nd^{3+}	3.88	6.92	10.0
Sm^{3+}	4.06	7.40	10.6
Eu^{3+}	4.07	7.48	10.6
Gd^{3+}	4.06	7.34	10.5
Tb^{3+}	4.15	7.62	10.6
Dy^{3+}	4.22	7.76	10.8
Ho^{3+}	4.22	7.72	10.7
Er^{3+}	4.28	7.86	10.9
Tm^{3+}	4.36	7.98	11.2
Yb^{3+}	4.43	8.12	11.3
Lu^{3+}	4.45	8.20	11.4
Y^{3+}	4.03	7.36	10.0

[a] At the 99% confidence level these values are in all cases better than ±0.02 for log β_1, ±0.04 for log β_2, and ±0.3 for log β_3.

The experimental conditions which were employed and the magnitude of the formation constants are such that the 1:1 and 2:1 complexes are quite well-defined and determined with good precision. The formation constants for the 3:1 complexes are, in general, much less certain. Additional complexes, such as an anionic 4:1 species, although their existence was indicated in the original calculations, have such large errors associated with their formation constants that it must be concluded that this study provides no evidence either for or against such species. In order to study species of this kind, an experimental technique in which the amount of picolinate ion in the solution could be increased would be necessary. Since this would necessitate operating at a higher ionic strength, such a study was not undertaken, particularly since we wish to compare these data with comparable studies at ionic strength 0.1 at which most measurements have been made.

In order to assess the reliability of our experimental technique the dissociation constant for acetic acid was determined. The value which was found [$2.75 \pm 0.01 \times 10^{-5}$, $t = 25°$, $\mu = 0.1\ M\ (KNO_3)$] is in good agreement with the values in the literature.[12,13]

Discussion

The formation constants of the 1:1 rare earth–picolinic acid complexes exhibit the trends which are characteristic of the majority of rare earth complexes with simple ligands which can act as chelating agents. The values of the constants increase quite uniformly as the atomic number increases. There is a small plateau at gadolinium (the "gadolinium break") and another small plateau at dysprosium and holmium. The position of yttrium is in the cerium earth region between neodymium and samarium.

The trends in the formation constants of the 2:1 complexes (log β_2 — log β_1) are parallel to those of the 1:1 complexes. Yttrium is more difficult to locate in this case but its position is between neodymium and samarium or gadolinium and terbium. The 3:1 complexes are somewhat peculiar in that in the cerium earth region the constants are almost of the same magnitude as the 2:1 constants and in two cases (cerium and neodymium) are slightly larger. As noted before, the experimental technique which was used led to large enough errors in the values of the 3:1 constants that it is not possible to determine whether this effect is real at the 99% confidence level or not.

Of primary concern in any discussion of complexes of this kind is the question of whether the heterocyclic nitrogen atom as well as the carboxyl group is coordinated. This question can be answered by examining some analogous compounds which have been studied previously. The most useful data to be examined are the formation constants of the rare earth complexes of acetic, glycolic, lactic, and α-hydroxyisobutyric acids. The data of Powell and his students[6,14] were chosen because they were determined at ionic strength 0.1.

The acetate complexes of the rare earths are simple mononuclear complexes of relatively low stability. The incorporation of a hydroxyl group into the molecule in the α-position decreases the basicity of the ligand but increases the stability of the resulting rare earth complex. Similar results are found for the lactate and α-hydroxyisobutyrate ligands. The preferred explanation for this effect at the present time is that the α-hydroxyl group also acts as a donor to the metal ion so that the ligand is bidentate and the complex is chelated.

A comparison of the formation constants of the rare earth–picolinic acid complexes with the ligands considered above shows that picolinic acid forms much more stable complexes and is also more basic. However, the picolinic acid complexes are so much more stable than the acetate complexes that there can be little doubt but that the ligand is bidentate, coordinating through both the nitrogen atom of the pyridine ring and the carboxyl group.

To confirm this conclusion an attempt was made to determine the formation constants of the nicotinic acid and acetic acid complexes of cerium and ytterbium using the same technique as for the picolinic acid system. In neither case, however, could reliable results be obtained. Both ligands formed complexes of the same order of magnitude but the formation constants were too small (log $K_1 \sim 2$) to be determined with any accuracy by our technique. Since nicotinic acid has an acid dissociation constant slightly smaller than acetic acid [pK for nicotinic acid = 4.67 as compared with pK for acetic acid = 4.56, both at $\mu = 0.1\ M\ (KNO_3)$ and determined in this study], the complexes which it forms should be of the same order of magnitude as the acetate complexes since chelation should also be impossible for nicotinic acid. Because the nicotinic acid complexes are so much

(12) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd Ed., Reinhold Publishing Corp., New York, N. Y., 1958, p. 676.

(13) R. S. Kolat and J. E. Powell, *Inorg. Chem.*, **1**, 293 (1962).

(14) R. H. Karraker, Ph.D. Dissertation, Iowa State University of Science and Technology, 1961.

weaker than those of picolinic acid, we feel that this is added confirmation that the nitrogen atom in picolinic acid is bound to the metal ion in these complexes. Moreover, since it has been shown that the predominant species in solutions of the pyridine carboxylic acids is that in which the nitrogen atom is protonated,[15] it would seem even more conclusive that the nitrogen atom is coordinated to the rare earth ion.

Although it would be of interest to compare the stabilities of the picolinic acid complexes with those of the corresponding glycine complexes, this is not possible since there are no reliable values for the glycine complexes. The available numbers,[2] however, can be considered to be upper estimates and a qualitative comparison can be made. When this is done, it is found that the picolinic acid complexes are the more stable, in agreement with similar observations for the alkaline earths.[7]

The reason for this enhancement of stability for the rare earth–picolinic acid complexes is possibly due to the fact that the heterocyclic ring fixes the closest distance of approach of the oxygen atoms of the carboxyl group to the nitrogen atom. Since models indicate that this distance is larger than for aliphatic compounds, such as glycine, this geometrical effect should favor coordination by the larger ions, such as the rare earths. This

(15) R. W. Green and H. K. Tong, *J. Am. Chem. Soc.*, **78**, 4896 (1956).

argument was suggested previously to account for the relative stabilities of the alkaline earth complexes.[7] The possibility of π-bonding in complexes of this kind cannot at present be ruled out but must await more detailed studies on related systems.

It is difficult to assess the relative donor capabilities of the pyridyl and hydroxyl groups because picolinic acid is considerably more basic than glycolic acid, which is used as a reference compound. Examination of the data given by Powell and his students for ligands containing the hydroxyl group would seem to indicate that the two groups have nearly the same effect on the formation constants. This is in agreement with the observations made previously on the ligands 2-picolyliminodiacetic acid and N-hydroxyethyliminodiacetic acid.[1]

Since the mercapto group apparently does not coordinate to the rare earth ions in the mercaptoacetic acid complexes, the pyridyl group is obviously a more effective donor to these ions.

Notes

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Reductions of Hexahalorhenate(IV) Salts with Alkali Metals in Liquid Ammonia[1]

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This paper reports the reductions of two hexahalorhenate(IV) salts with alkali metals in anhydrous liquid ammonia at the boiling point of the solutions. In one product we have found a hydridorhenate like that recently characterized by Ginsberg and coworkers.[2]

Experimental

Apparatus.—The liquid ammonia reactions were carried out in a type of apparatus described previously.[3] Generally, between 0.2 and 1.5 g. of hexahalorhenate(IV) salt was put in the reactor, dissolved in 40–50 ml. of ammonia, and alkali metal added in excess.

Infrared spectra were recorded of products in potassium bro-

(1) Part of this work is from the master's thesis of C. L. Ottinger, The University of Tennessee, Knoxville, Tenn., Dec., 1954.

(2) (a) A. P. Ginsberg, J. M. Miller, and E. Koubek, *J. Am. Chem. Soc.*, **83**, 4909 (1961); (b) S. C. Abrahams, A. P. Ginsberg, and K. Knox, *Inorg. Chem.*, **3**, 558 (1964).

(3) G. W. Watt and C. W. Keenan, *J. Am. Chem. Soc.*, **71**, 3833 (1949).

mide pellets with a Perkin-Elmer Infracord. Pellet mixes were loaded into the pellet press in a gloved bag. During the recording of two consecutive spectra the pellets were bathed with a stream of dry nitrogen. Only in the case of potassium amide did the second spectrum differ appreciably from the first.

Preparation of K_2ReCl_6.—Potassium hexachlororhenate(IV) was prepared according to the method of Hurd and Reinders.[4]

Anal. Calcd. for K_2ReCl_6: Cl, 44.6; Re, 39.0. Found: Cl, 44.3; Re, 39.6.

Exposure of K_2ReCl_6 to NH_3.—Samples of potassium hexachlororhenate(IV) were dissolved in liquid ammonia and allowed to stand for several hours at about $-33°$. Weights of three samples initially and after recovery, respectively, were: 0.5115 g., 0.5210 g.; 0.3027 g., 0.3108 g.; and 0.6547 g., 0.6601 g. The 35-line X-ray diffraction pattern for one residue was practically identical with that for the original K_2ReCl_6. No loss or gain of lines was noted. Some samples of K_2ReCl_6 on longer standing in ammonia, and with delayed evacuation, became discolored.

Preparation of $(NH_4)_2ReBr_6$.—Ammonium hexabromorhenate(IV) was prepared by an adaptation of the method of Rulfs and Meyers.[5]

Anal. Calcd. for $(NH_4)_2ReBr_6$: NH_4^+, 5.1; Re, 26.5; Br, 68.3. Found: NH_4^+, 4.7; Re, 26.0; Br, 67.7.

Exposure of $(NH_4)_2ReBr_6$ to NH_3.—One sample of ammonium hexabromorhenate(IV) weighing 77.1 mg. was dissolved in ammonia at $-33°$. The ammonia was allowed to evaporate slowly, leaving a brilliant yellow solid behind. On being carefully evacuated at room temperature the solid began to turn orange and maintained this color as constant weight was attained. An X-ray

(4) L. C. Hurd and V. A. Reinders, *Inorg. Syn.*, 1, 178 (1939).

(5) C. L. Rulfs and R. J. Meyers, *J. Am. Chem. Soc.*, **77**, 4505 (1955).