Nitrogen and Oxygen Exchange between Hydroxopentaamminecobalt(III) and Solvent Species in Aqueous Ammonia. Uncatalyzed Exchange[1]

Theodore J. Williams and John P. Hunt[2]

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Abstract: Using mass spectrometric techniques, the exchange of ammonia between $Co(NH_3)_5OH^{2+}$ and aqueous ammonia was studied as a function of temperature and complex, ammonia, and hydrogen ion concentrations. The effect of changing surface area and molecular oxygen content available to the reactants was also observed. A few measurements of oxygen-exchange rates were also made for comparative purposes. A simple first-order rate law, rate = $k[Co(NH_3)_5OH^{2+}]$, was demonstrated for ammonia exchange. A comparison of the ammonia and oxygen exchange data and a consideration of related systems suggested a single dissociative rate-determining step for both exchange mechanisms with competition for the intermediate by nitrogen- and oxygen-containing solvent species.

Hydroxopentaamminecobalt(III) is expected to exchange its ligands very slowly. Studies of ammonia exchange between $Co(NH_3)_6^{3+}$ and aqueous ammonia give a rate constant of *ca.* 10^{-10} sec^{-1} at 25° for this reaction.[3] The lack of decomposition and oxygen exchange in *trans*-$Co(en)_2NH_3OH^{2+}$ for the length of time the isomerization reaction of this complex was observed[4] suggests that exchange in this case would have a rate constant of certainly less than 10^{-7} sec^{-1} at 30°. Furthermore, the rates of oxygen exchange for $Co(NH_3)_5H_2O^{3+}$ measured as a function of acidity suggested an upper limit for the specific rate constant for oxygen exchange in $Co(NH_3)_5OH^{2+}$ of 1.4×10^{-7} sec^{-1} at 25°.[5] Although quite slow, the rates of nitrogen exchange between bound ammonia and free solvent ammonia were measurable, and a study of this exchange reaction was undertaken. Rates of oxygen exchange were also measured for comparison with some of the ammonia exchange data in hopes of clarifying the mechanism.

Experimental Section

Reaction Procedure. With the exception of the aquopentaamminecobalt(III) perchlorate salt, all the chemicals used were commercial products of analyzed reagent grade. The complex salt was prepared by the hydrolysis of carbonatopentaamminecobalt(III) nitrate using perchloric acid[6] and was analyzed for cobalt and nitrogen.

Anal. Calcd for $[Co(NH_3)_5H_2O](ClO_4)_3$: Co, 12.5; N, 15.23. Found: Co, 12.4; N, 15.15.

The pH of a particular reaction solution was determined by buffering with NH_4NO_3, and the ionic strength was adjusted to 2.28 *M* in each reaction solution using $NaNO_3$. The solutions were enriched in nitrogen-15 or oxygen-18 using either NH_4NO_3 (9.5 atom % ^{15}N), purchased from Eastman Organic Chemicals, Distillation Products Division, or enriched water (1.52 atom % ^{18}O), obtained from the Weizmann Institute, Rehovoth, Israel. In all cases the enrichment used in the reaction solution was 10–15% above the natural abundance.

The reaction solutions were made up in an apparatus which could be attached to a vacuum line and which had two compartments separated by a stopcock. The complex and ammonia solutions were initially placed in the separate compartments and, in most cases, degassed by repeated freezing with liquid nitrogen, evacuation to maximum vacuum, and then thawing. The solutions were then brought to the desired temperature in a constant-temperature bath and mixed. For all samples the reaction vessels were covered with aluminum foil to keep out light and were kept at constant temperature (±0.1°) for the reaction period. Individual samples were used for each time interval, and at least three experimental points were usually taken in the determination of each rate. At the end of the desired time of reaction the cobaltic complex was recovered from the reaction solution as $[Co(NH_3)_5H_2O]Br_3$ by precipitation with cold 50% hydrobromic acid. For nitrogen-exchange measurements the precipitate was washed with *ca.* 15% hydrobromic acid and then alcohol. The remaining compound was then wrapped in the filter paper used for the filtration and stored. There was some slow conversion to the bromopentaamminecobalt(III) bromide during long periods storage, but this did not appear to affect the exchange results. For the oxygen-exchange experiments, the precipitate was washed once with *ca.* 10% hydrobromic acid, three times with absolute ethanol, and three times with anhydrous ether. It was then dried for 24 hr in a vacuum desiccator.

Experiments were done to determine the effect of surface area and atmospheric oxygen on the nitrogen-exchange rate. The surface area was changed by using glass beads for which the average area per gram of beads was determined. The oxygen content of the reaction solution was varied by varying the degassing procedure.

Measurement of Isotopic Abundance. After precipitation the nitrogen or oxygen contained in the complex was converted to nitrogen gas or carbon dioxide.[7,8] To produce the nitrogen required for mass spectrometer analysis, another apparatus was used which could also be attached to the vacuum line. It consisted of two flasks joined by glass-tapered joints in such a manner that one flask could be tipped and its content emptied into the other. The bromide precipitate was first treated with a Kjeldahl procedure to form an ammonium ion solution in one flask of the apparatus. A hypobromite solution was added to the other flask, and both solutions were degassed separately. The solutions were then mixed after cooling them with an ice bath. When the oxidation of the ammonium ion to nitrogen was complete, the solution was frozen with liquid nitrogen and the nitrogen formed by the oxidation was transferred to mass spectrometer sample tubes using a Toepler pump. Carbon dioxide was prepared by first heating the precipitate (110°) to remove the complexed water. This water was then heated with $Hg(CN)_2$ (400°). In both cases the reactions were carried out in evacuated capsules which were opened in the vacuum line for transfer of the product gases. The CO_2 formed was purified by first freezing with liquid nitrogen, evacuating the noncondensable gases, and then passing the retained gases through a trap

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(1) This work was supported by U. S. AEC Contract AT-(45-1)-2040 and is report No. RLO-2040-5.

(2) To whom inquiries should be addressed.

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(8) M. Anbar and S. Guttman, *Intern. J. Appl. Radiation Isotopes*, 5, 223 (1959).

cooled with an ethyl bromide slush (−120°) into a mass spectrometer sample tube.

Mass spectrometric analysis of the N_2 and CO_2 was done with a Nuclide Analysis Model RMS-5 mass spectrometer. The isotopic ratios of ^{15}N to ^{14}N and ^{18}O to ^{16}O were measured with an instrument reproducibility of ±0.1%. For each measurement on exchange samples corresponding ratios were measured for standard samples containing the natural isotopic abundances. This was done to correct for fluctuations in the instrument's performance between measurements.

In most systems the reactions were followed to 40–60% exchange. The ammonia exchange rate measurement at 25° was followed to *ca.* 8% and should be considered as only an estimate of the rate.

Spectrophotometric Measurements. Solutions approximating the extremes for the conditions used in the kinetic experiments were studied spectrophotometrically to detect changes in the system during the time the exchange reactions were followed. Measurements of absorbance were done as a function of time for various temperatures and concentrations. In all spectrophotometric experiments the absorbances were measured at selected wavelengths between 650 and 350 mμ using a Beckman Model DU spectrophotometer.

Results

Treatment of the Data. The measured ratios were adjusted relative to the same standard and then used to find the atom fraction, α, of ^{15}N or ^{18}O in each sample. The relation

$$\alpha = r/(2 + r)$$

can be derived from the probabilities for the random pairing of atoms where $r = (^{29}N_2)/(^{28}N_2)$ or $r = (^{46}CO_2)/(^{44}CO_2)$. In this manner the atom fraction for each time interval, α_t, was found. The fraction at zero time, α_0, was found from measurements on the unreacted complex, and the fraction at infinite time, α_∞, was found from measurements on the total reaction solution or was calculated from known atom fractions of both the complex and the enriched stock ammonia solutions. This procedure for finding α ignores any isotope effects and may produce a 1–2% error in the measured rates.

After each time interval the fraction of exchange, F, was calculated from the expression

$$F = (\alpha_t - \alpha_0)/(\alpha_\infty - \alpha_0)$$

Using F, the rates of exchange were found by the usual McKay treatment for simple, homogeneous, isotopic exchange.[9] The equation used to calculate the rate of exchange is

$$\text{rate} = \frac{(a)(b)0.693}{(a + b)t_{1/2}}$$

The half-time for the exchange reaction, $t_{1/2}$, was found from a plot of log $(1 - F)$ against time at $1 - F = 0.5$. The concentrations of the exchanging atoms in each environment are given by a and b. For nitrogen exchange a = 5[Co(III)], where 5 is the number of ammonia ligands in the complex assumed to be exchanging, and $b = ([NH_3] + [NH_4^+])$. For oxygen exchange a = [Co(III)] and $b = [H_2O]$, and since $[H_2O] \gg$ [Co(III)] the rate equation reduces to

$$\text{rate} = [\text{Co(III)}]0.693/t_{1/2}$$

The average deviation in the half-times found for pairs of experimental points including the $F = 0$ intercept on each McKay plot was less than ±4%. In most cases the plots showed excellent linearity, indicating that the rates were reproducibly measured since separate samples were used for each experimental point. The lack of curvature also supports the idea that all five ammonia ligands are exchanging at equivalent rates. Curvature may not, however, be apparent until the exchange reaches $F = 0.8$ for the instance where ammonia *cis* to the hydroxo ligand is exchanging more rapidly than *trans*.

Results of the Kinetic Studies. The spectrophotometric experiments showed no significant changes in the reaction solutions in the times for which exchange was followed. For measurements at 55° and 1.0 M NH_3 a slow conversion to the hexaamminecobalt(III) complex was indicated, but the initial rate of conversion was estimated to be less than 1% per day. This rate is slow enough to permit a valid McKay treatment within the estimated 4–5% experimental error for this method of rate measurement.

Changing surface area and oxygen content available to the reactants showed that the rate of nitrogen exchange is not significantly catalyzed by either factor. The differences in the per cent exchange for a particular reaction solution at the same time were the same within experimental error for surface areas from 35 to 370 cm² and a variation in the number of times the solutions were degassed from 0 to 3.

The results of the nitrogen or ammonia exchange rate measurements are presented in Table I. The Co(III) concentrations given in Table I are for the total amount of aquo complex added to the reaction solution. The acid dissociation constant for the aquo complex (pK = 5.7 at 15° and zero ionic strength)[10] indicates that the conversion to the hydroxo form of the complex is virtually complete at the pH of these ammonia solutions (pH 8–9). The other concentrations given in Table I were calculated from concentration product constants given as functions of ionic strength and temperature.[11]

Table I. Ammonia Exchange Results[a]

Expt no.	Temp, °C	$[NH_3]$, M	$[H^+] \times 10^{-9}$ M	$t_{1/2}$, hr	Rate × 10^4 M/hr	$k \times 10^6$[g] sec⁻¹
1	25.0	0.29	1.03	2100	0.61	0.39
2	35.5	0.29	2.36	397	3.2	2.06
3	35.5	0.65	1.05	423	3.1	2.00
4	35.5	0.91	0.75	403	3.3	2.13
5[b]	35.5	0.65	0.58	382	3.3	2.13
6[c]	35.5	0.65	1.54	435	3.1	2.00
7[d]	35.5	0.65	1.96	415	3.3	2.13
8[e]	44.4	0.62	2.32	90.0	23.6	8.9
9[f]	44.4	0.67	2.04	102	6.4	8.9
10	44.4	0.29	4.79	86.4	14.7	9.5
11	44.4	0.65	2.13	92.9	14.1	9.1
12	44.4	0.91	1.52	91.7	14.5	9.4
13	55.2	0.29	12.3	15.8	80.4	50.2
14	55.2	0.65	5.47	17.3	75.8	48.9
15	55.2	0.91	3.90	17.4	76.7	49.5

[a] Unless otherwise indicated, [Co(III)] = 0.043 M, $[NH_4^+]$ = 0.98 M, and the ionic strength is adjusted with $NaNO_3$ to 2.28 M. [b] $[NH_4^+]$ = 0.54 M. [c] $[NH_4^+]$ = 1.44 M. [d] $[NH_4^+]$ = 1.84 M. [e] $[NH_4^+]$ = 1.01 M, [Co(III)] = 0.065 M. [f] $[NH_4^+]$ = 0.96 M, [Co(III)] = 0.020 M. [g] k is found from rate = k[Co(III)].

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(9) O. E. Myers and R. J. Prestwood, "Radioactivity Applied to Chemistry," A. C. Wahl and N. A. Bonner, Ed., John Wiley and Sons, Inc., New York, N. Y., 1951, p 6.

(10) R. S. Young, "Cobalt," Reinhold Publishing Corp., New York, N. Y., 1960, p 111.

(11) J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, Denmark, 1941, pp 278–285.

The data taken for ammonia exchange demonstrate that the exchange reaction follows a simple first-order rate law, rate = $k[Co(NH_3)_5OH^{2+}]$. The specific rate constants in Table I were calculated from this rate law. Considering these constants, experiments 8–10 show the first-order dependence of the rate on complex concentration, experiments 3 and 5–7 illustrate the lack of dependence on hydrogen ion concentration, and the other experiments demonstrate that the rate of exchange is essentially independent of ammonia concentration for each of the temperatures 35.5, 44.4, and 55.2°. The rate constants given in Table I exhibit standard deviations of 0.06, 0.3, and 0.7 at the temperatures 35.5, 44.4, and 55.2°, respectively.

Using the averages for the rate constants at each temperature, a nonlinear least-squares program gave the activation parameters, $\Delta H^{\ddagger} = 32 \pm 1$ kcal mole^{-1} and $\Delta S^{\ddagger} = 18 \pm 6$ eu at 35.5°, for ammonia exchange.

The results of the rate measurements for oxygen exchange are contained in Table II. The limited data indicate that the rate may be independent of pH and ammonia concentration and therefore suggest that the rate law for oxygen exchange may have the same simple form as for ammonia exchange. A plot of log (k sec^{-1}/T°K) *vs.* 1/T°K, assuming the first-order rate law, was made which showed some curvature. A least-squares calculation gave the apparent activation parameters, $\Delta H^{\ddagger} = 27 \pm$ kcal mole^{-1} and $\Delta S^{\ddagger} = 4 \pm 2$ eu at 35.5°. The difference in rates and their temperature dependence for the two types of exchange suggests that the mechanisms for nitrogen and oxygen exchange differ.

Table II. Oxygen Exchange Results[a]

Expt no.	Temp, °C	$[NH_3]$, *M*	$t_{1/2}$, hr	Rate × 10^4 *M*/hr	$k \times 10^6$ [b] sec^{-1}
16	55.2	0.29	12.5	24	16
17	44.4	0.29	55.5	5.4	3.5
18	35.5	0.29	180	1.7	1.1
19	35.5	0.65	180	1.7	1.1

[a] For all samples [Co(III)] = 0.043 *M*, $[NH_4^+]$ = 0.98 *M*, and the ionic strength was adjusted with $NaNO_3$ to 2.28 *M*. [b] k is found from rate = k[Co(III)].

Discussion

Rate Comparison. The increase in the rate of ammonia exchange for $Co(NH_3)_5OH^{2+}$ relative to the hexaammine complex is consistent with the general labilizing influence exhibited by the hydroxo ligand relative to ammonia. It has been especially noted in the hydrolysis of cobaltic complexes of the type $Co(en)_2LCl^+$ that the rate is at a minimum for L = NH_3 and much faster for L = OH^-.[12] This work[12] also suggests that OH^- facilitates the dissociation of ligands *cis* to it more effectively than those in the *trans* position. Although the experimental evidence for ammonia exchange with $Co(NH_3)_5OH^{2+}$ does not reveal this *cis* effect, it does rule out a significant *trans* labilization.

Oxygen exchange for complexes similar to $Co(NH_3)_5OH^{2+}$ suggests that the measured rates of exchange shown in Table II are more rapid than expected.[4] However, the rate constant for oxygen exchange with $Co(NH_3)_5OH^{2+}$ calculated for 25°, 2×10^{-7} sec^{-1}, does compare favorably with the suggested upper limit at 25°, 1.4×10^{-7} sec^{-1}.[5]

Mechanistic Considerations. Both the observed rate laws and the entropies of activation support a dissociative type mechanism for either oxygen or nitrogen exchange. The differences in the rates of exchange could be explained by postulating separate mechanisms of the type

$$Co(NH_3)_5OH^{2+} \rightleftharpoons Co(NH_3)_5{}^{3+} + OH^-$$
$$Co(NH_3)_5{}^{3+} + {}^*OH^- \rightleftharpoons Co(NH_3)_5{}^*OH^{2+}$$

and

$$Co(NH_3)_5OH^{2+} \rightleftharpoons Co(NH_3)_4OH^{2+} + NH_3$$
$$Co(NH_3)_4OH^{2+} + {}^*NH_3 \rightleftharpoons Co(NH_3)_4{}^*NH_3OH^{2+}$$

The apparent difference in $\Delta H^{\ddagger}$ for oxygen and ammonia exchange could then be rationalized by simply considering the ammonia to be more strongly bonded to the metal than the hydroxo ligand. There are a number of factors which contradict separate mechanisms, particularly that postulated for oxygen exchange. Most importantly, the selectivity of the two five-coordinate intermediates that this requires seems very unrealistic. Indiscriminate reaction of the two types of intermediates would result in the formation of the very stable $Co(NH_3)_6{}^{3+}$, which does not appear in the reaction products, and $Co(NH_3)_4(OH)_2{}^+$.

Another approach, which is perhaps more consistent with the previous observations, is to consider that both types of exchange are predominantly governed by the same rate-determining process

$$Co(NH_3)_5OH^{2+} \rightleftharpoons Co(NH_3)_4OH^{2+} + NH_3$$

This intermediate is favored relative to $Co(NH_3)_5{}^{3+}$ by possible π-bonding stabilization by the hydroxo ligand and need not result in the decomposition of the complex in the presence of ammonia. The rate differences for oxygen and nitrogen exchange must then be explained by subsequent steps in the mechanism,

A general mechanism for both nitrogen and oxygen exchange is given by the equilibria

$$Co(NH_3)_5OH^{2+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Co(NH_3)_4OH^{2+} + NH_3$$

$$Co(NH_3)_4OH^{2+} + OH^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Co(NH_3)_4(OH)_2{}^+$$

The presence of $Co(NH_3)_4(OH)_2{}^+$ was not detected spectrophotometrically, and equilibrium considerations by Bjerrum[11] for the cobaltic ammines show that the pentaammine is much more stable than the tetraammine at ammonia concentrations as low as 0.3 *M*.

The exchange rate for ammonia is then $R_N = k_1 \cdot [Co(NH_3)_5OH^{2+}]$. The oxygen exchange rate is taken to be equivalent to the rate of formation of the dihydroxotetraamminecobalt(III) species

$$R_O = k_2[Co(NH_3)_4OH^{2+}][OH^-]$$

Oxygen-exchange rates measured for the analogous species, $Co(en)_2(OH)_2{}^+$,[13] indicate that the tetraammine would undergo complete isotopic mixing in the time of ammonia exchange in the pentaammine. Using a steady-state treatment and neglecting terms containing

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(12) M. L. Tobe, *Sci. Progr.*, **48**, 484 (1960).

(13) W. Kruse and H. Taube, *J. Am. Chem. Soc.*, **83**, 1280 (1961).

the minor species, $Co(NH_3)_4(OH)_2^+$, one obtains

$$R_O = \frac{k_1[Co(NH_3)_5OH^{2+}]k_2[OH^-]}{k_{-1}[NH_3] + k_2[OH^-]}$$

If $k_{-1}[NH_3] > k_2[OH^-]$ this reduces to

$$R_O = \frac{k_1k_2[Co(NH_3)_5OH^{2+}][OH^-]}{k_{-1}[NH_3]}$$

In our experiments the ratio $[OH^-]/[NH_3]$ was held constant, leading to the apparent first-order rate law. The lower rate for oxygen exchange would then be due to low hydroxide ion concentration. Using the rate ratios, R_N/R_O, a calculation of the ratio k_2/k_{-1} at 35.5° gives a value of *ca.* 4×10^4.

If the major species, H_2O, is considered in place of OH^- in the previous mechanism, a similar calculation gives $k_{-1} \approx 300k_2$. Why water should be less reactive than ammonia is not clear to us, but if oxygen exchange is due only to the reaction of the intermediate with water, this is the apparent conclusion.

The above rate law for oxygen exchange is consistent with the difference in activation enthalpy for oxygen and nitrogen exchange and some curvature in the Arrhenius plot of the oxygen data.

It would be desirable to obtain more data on the oxygen-exchange reaction for the pentaammine as well as for nitrogen and oxygen exchange in the tetraammine.

Nitrogen and Oxygen Exchange between Hydroxopentaamminecobalt(III) and Solvent Species in Aqueous Ammonia. II. Cobalt(II)-Catalyzed Exchange[1]

Theodore J. Williams and John P. Hunt[2]

Contribution from the Department of Chemistry, Washington State University, Pullman, Washington 99163. *Received July 29, 1968*

Abstract: The effect of the electron-transfer reaction between $Co(NH_3)_5OH^{2+}$ and cobaltous ammines on the nitrogen and oxygen exchange between the cobaltic pentaammine and solvent species was observed by measuring these exchange rates in aqueous solutions of ammonia and Co(II). Previously measured electron-transfer rates were also remeasured using a different experimental technique. The rates of electron transfer and catalyzed nitrogen exchange were shown to follow the rate law, rate = $k[Co(NH_3)_5OH^{2+}][Co(NH_3)_5^{2+}]$. The lack of catalysis of oxygen exchange by Co(II) demonstrated a hydroxo-bridged mechanism for electron transfer. The rates of catalyzed nitrogen exchange were slower, relative to the electron-exchange rates, than expected for a simple hydroxo-bridged mechanism. This suggested the possibility of multiple bridging in the activated complex.

The electron-transfer reaction between $Co(NH_3)_5OH^{2+}$ and cobaltous ammine species, $Co(NH_3)_n^{2+}$, in aqueous ammonia solutions has been studied briefly using ^{60}Co as a tracer to measure the rates of cobalt exchange for various conditions.[3] A comparison of this reaction with the electron-transfer behavior in the $Co(NH_3)_6^{3+}$–$Co(NH_3)_n^{2+}$ system under similar conditions[4] suggests that it might proceed through a bridged intermediate in which the proposed activated complex is the symmetrical species, $(NH_3)_5Co\text{-}OH\text{-}Co(NH_3)_5^{4+}$. In support of this hypothesis, the rate law for the electron-transfer reaction appeared to have the form

$$\text{rate} = k[Co(NH_3)_5OH^{2+}][Co^{2+}][NH_3]^5$$

To more clearly elucidate aspects of the mechanism for electron exchange in this system, a study was made of the effect of the electron-exchange reaction on the exchange of the ammonia and hydroxide ligands in the cobaltic complex. The rates of nitrogen and oxygen exchange promoted by the electron transfer were found using the data in part I of this work.[5] The previously measured rates of cobalt exchange were also checked using a different method of removing oxygen from the reaction solution and a different separation procedure.

Experimental Section

Spectrophotometric Studies and Solution Composition. Spectra were taken in an attempt to detect any species formed by the combination of the cobaltic and cobaltous complexes. In an apparatus similar to that described in part I for preparing reaction solutions, solutions were prepared by separately degassing ammonia and $Co(NO_3)_2 \cdot 6H_2O$ and/or $[Co(NH_3)_5H_2O](ClO_4)_3$ solutions. The solutions were then mixed and transferred to an attached, evacuated, quartz 1-mm cell obtained from the Pyrocell Manufacturing Co. The cobaltous nitrate was a commercial product and the cobaltic complex was the same as that used in part I. The 1-mm cell was purchased with quartz to Pyrex sealed tubing to which a stopcock and taper joint were added. The spectra of solutions containing both Co(II) and $Co(NH_3)_5OH^{2+}$ were compared to the sum of absorbances of the analogous solutions containing either only Co(II) or $Co(NH_3)_5OH^{2+}$. The spectra were measured with a Cary Model 14 spectrophotometer.

Spectral experiments were done on acidified reaction solutions to observe changes in the solution as a result of the electron-transfer reaction. A reaction carried out at 35.5° and 0.33 *M* NH_3 was acidified at 80% exchange, and its spectrum was compared with the sum of the absorbances of analogous acidified solutions containing

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(1) This work supported by U. S. AEC Contract AT-(45-1)-2040 and is report No. RLO-2040-6.

(2) To whom inquiries should be addressed.

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(4) N. S. Biridar, D. R. Stranks, and M. S. Vaidya, *Trans. Faraday Soc.*, **58**, 2421 (1962).

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