Reactions of Complex Compounds of Cobalt. Part IX.[1] Ammonia Exchange during the Base Hydrolysis of Chloropenta-amminecobalt(III) Ion in Concentrated Aqueous Ammonia

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In unsuccessful attempts to detect kinetically labile cobalt(II) species (intermediates in a postulated redox mechanism) the ammonia exchange during base hydrolysis of $[Co(^{15}NH_3)_5Cl]Cl_2$ in concentrated aqueous ammonia was examined. At *ca.* 23 °C there was less than 1% exchange. $^{15}N/^{14}N$ analyses were done by a novel method using ^1H magnetic resonance. Experimental details are given.

THE mechanism of hydrolysis by base of cobalt(III) ammines has been discussed with regard to several possible schemes [2-6] of which S_N1CB is most widely accepted.[5] A suggested redox mechanism [4] has aroused some interest [5-9] and in an attempt to evaluate it, we have undertaken the exchange studies reported in this paper. Applied to chloropenta-amminecobalt(III) ion, the redox mechanism may be summarised as in reactions (1)—(4).

$$[Co^{III}(NH_3)_5Cl]^{2+} + OH^- \rightleftharpoons \{[Co^{III}(NH_3)_5Cl]OH\}^+ \quad (1)$$

$$\{[Co^{III}(NH_3)_5Cl]OH\}^+ \rightleftharpoons \{[Co^{II}(NH_3)_5Cl]HO\cdot\}^+ \quad (2)$$

$$\{[Co^{II}(NH_3)_5Cl]HO\cdot\}^+ \rightleftharpoons \{[Co^{II}(NH_3)_5]HO\cdot\}^{2+} + Cl^- \quad (3)$$

$$\{[Co^{II}(NH_3)_5]HO\cdot\}^{2+} \rightleftharpoons [Co^{III}(NH_3)_5OH]^{2+} \quad (4)$$

Formation of an ion pair [step (1)] is followed by electron transfer from OH^- to Co^{III} to give a radical-ion pair containing $\cdot OH$ and Co^{II} [step (2)]; after expulsion of chloride ion yielding a 5-co-ordinate intermediate [step (3)], oxidation and completion of the co-ordination shell occur in a single final step. This mechanism and some observations rationalized by it have been discussed in detail.[4]

Scrambling of the ammine ligands of *trans*-$[Co(^{14}NH_3)_4(^{15}NH_3)X]^{2+}$ (X = Cl, Br, or NO_3) during base hydrolysis has been explained [10] in terms of a common cobalt(III) intermediate whose stereochemistry could not be satisfactorily deduced (the isomer ratios of the product do not fit the predicted statistical pattern for an intermediate with either square pyramidal or trigonal bipyramidal structure). These results could alternatively be interpreted as showing a kinetically labile cobalt(II) [4,11-13] intermediate, whose lifetime was sufficient to allow redistribution of the ammonia molecules within the co-ordination sphere of the metal ion. Indeed, if this lifetime were long enough, co-ordinated ammonia might exchange with any potential ligand in the immediate neighbourhood of the reactive intermediate. Under the usual conditions of base hydrolysis, such potential ligands are water and hydroxide ion (which could provide a route for the displacement of co-ordinated ammonia commonly observed with cobalt(III) amines in basic solution [4]). However, in the presence of free ammonia, the probability of exchange is increased, since ammonia is a good ligand for both cobalt(II) and cobalt(III). By use of $[^{15}N]$ammonia we have defined the limits of ammonia exchange as a comment on the nature of the intermediates in base hydrolysis of $[Co(NH_3)_5Cl]Cl_2$ and $[Co(NH_3)_5(acetate)](NO_3)_2$, convenient substrates with only one readily hydrolysable ligand and simple stereochemistry.

RESULTS

$[Co(^{15}NH_3)_5Cl]Cl_2$ of 99·1% enrichment was allowed to react in concentrated aqueous ammonia of natural isotopic abundance ([uncomplexed NH_3] = *ca.* 14M and $[H_2O]$ = *ca.* 36M). The uncomplexed ammonia was removed, and $[Co(NH_3)_6]^{3+}$ ion (*ca.* 12% yield) and $[Co(NH_3)_5Cl]^{2+}$ (*ca.* 5% yield) removed by chromatography. The co-ordinated ammonia in $[Co(NH_3)_5OH]^{2+}$ was analysed for ^{15}N by a ^1H n.m.r. method, described in detail in the Experimental section.

The percentage of ^{15}N in the nitrogen of $[Co(NH_3)_5OH]^{2+}$ was found to have fallen by *ca.* 1% relative to that in $[Co(NH_3)_5Cl]^{2+}$ (see Table 1). Application of the Student t-test [14] confirmed that the difference in the isotope fractions before and after base hydrolysis is highly significant (the 0·1% probability level is reached). The percentage of ^{15}N in the nitrogen of $[Co(NH_3)_6]^{3+}$ isolated from the same reaction mixture (82·28 ± 0·84%) agreed with the value calculated for incorporation of one $^{14}NH_3$ ligand into [99·1% ^{15}N]-penta-amine (82·64%). Thus, within our experimental error, no exchange of ammonia with hexa-ammine or its precursors was detected. The quantity of $[Co(NH_3)_5Cl]^{2+}$ recovered from the reaction mixture was too small to permit ^{15}N analysis by our method.

In further experiments, $[Co(NH_3)_5Cl]Cl_2$ and $[Co(NH_3)_5(acetate)](NO_3)_2$ of natural isotopic abundance were each allowed to react with aqueous sodium hydroxide in the

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[2] F. Basolo and R. G. Pearson, 'Mechanism of Inorganic Reactions,' 2nd edn., Wiley, New York, 1967.

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[12] T. J. Swift and R. E. Connick, *J. Chem. Phys.*, 1962, **37**, 307.

[13] J. Bjerrum and K. G. Poulsen, *Nature*, 1952, **169**, 463.

[14] M. J. Moroney, 'Facts from Figures,' Penguin Books, Harmondsworth, 1951, p. 232.

presence of 30% enriched [^{15}N]ammonium sulphate. No ammonia exchange was detected (see Table 1).

DISCUSSION

The observed difference in ^{15}N-content between $[Co(^{15}NH_3)_5Cl]Cl_2$ and the product of its hydrolysis in concentrated [^{14}N]ammonia solution may arise in several ways.

(1) *Uncomplexed Ammonia in the Purified Solution of* $[Co(NH_3)_5OH]Cl_2$.—Such contamination could arise from the atmosphere, the chromatographic column, the reagents, the eluting solution or from failure to remove completely the ammonium chloride formed as a byproduct. However, tests with Nessler's solution show the absence of unco-ordinated ammonia in concentrations sufficient to be detected by our analytical method.

TABLE 1

Percentage of ^{15}N in the nitrogen of co-ordinated ammonia before and after base hydrolysis in the presence of uncomplexed ammonia. Quoted errors equal the standard deviation

Reactant: %^{15}N	Products %^{15}N	Reaction conditions
$[Co(NH_3)_5Cl]Cl_2$ $99{\cdot}22 \pm 0{\cdot}20$	(*a*) $[Co(NH_3)_5OH]^{2+}$ $98{\cdot}41 \pm 0{\cdot}11$ separate $98{\cdot}04 \pm 0{\cdot}19$ experiments (*b*) $[Co(NH_3)_6]^{3+}$ $82{\cdot}28 \pm 0{\cdot}84$	$[Co] = 0{\cdot}0096$M $[NH_3] = 14{\cdot}3$M, natural-abundance ^{15}N pH = *ca.* 12·2 *ca.* 23 °C 45 min
$[Co(NH_3)_5Cl]Cl_2$ 0·37	$[Co(NH_3)_5OH]^{2+}$ 0·4 } separate 0·36 } experiments 0·38 }	$[Co] = 0{\cdot}012$M $[NaOH] = 0{\cdot}0153$M $[(NH_4)_2SO_4] = 0{\cdot}064$M, 30% ^{15}N *ca.* 23 °C 30 min
$[Co(NH_3)_5(acetate)](NO_3)_2$ 0·37	$[Co(NH_3)_5OH]^{2+}$ natural abundance	$[Co] = 0{\cdot}008$M $[NaOH] = 0{\cdot}114$M $[(NH_4)_2SO_4] = 0{\cdot}048$M, 30% ^{15}N *ca.* 0 °C 60 min

(2) *Extraneous Complexed Ammonia.*—Our chromatographic procedure separates $[Co(NH_3)_5OH]^{2+}$ from $[Co(NH_3)_6]^{3+}$ and $[Co(NH_3)_5Cl]^{2+}$. No minor product was observed, but tetra-ammines or hydroxo-bridged polynuclear species would be removed by this procedure. $[Co(NH_3)_5OH]^{2+}$ could be formed by base hydrolysis of $[Co(NH_3)_6]^{3+}$ and then collected in the same chromatographic fraction as $[Co(NH_3)_5OH]^{2+}$ formed directly from $[Co(NH_3)_5Cl]^{2+}$. However, this possibility is ruled out by the observed stability of $[Co(NH_3)_6]^{3+}$ in concentrated ammonia and by the reported stability of solutions in sodium hydroxide.[15,16]

(3) *Exchange in the Starting Complex or Product.*—$[Co(NH_3)_6]^{3+}$ undergoes slow exchange in aqueous ammonia,[17] but does not exchange in ammonium nitrate solution unless cobalt(II) or charcoal is present.[16] We know of no report of exchange in penta-amminecobalt(III) complexes, but a very approximate extrapolation * of the results on $[Co(NH_3)_6]^{3+}$ suggests that exchange in penta-ammines might be of the order of magnitude necessary to account for our observations (*ca.* 0·4%). In the presence of catalytic traces of cobalt(II) more exchange is expected, especially since electron transfer from $[Co(NH_3)_n]^{2+}$ is much more rapid to $[Co(NH_3)_5OH]^{2+}$ than to $[Co(NH_3)_6]^{3+}$ (the rate constants at 64·5 °C are 9×10^{-4} and 10^{-9} l mol^{-1} respectively).[18]

(4) *Exchange of Ammonia as a Consequence of Base Hydrolysis.*—This is a result of the reactivity of the kinetically labile cobalt(II) species implicit in the redox mechanism. Even if it is assumed that the observed incorporation of $^{14}NH_3$ arises entirely from this cause, the lifetime of the cobalt(II) species is unlikely to exceed 3×10^{-10} s [*i.e.*, the time required for 1% exchange of cobalt(II) ammines in aqueous 14M-ammonia, estimated by use of the exchange rate:[11] 3×10^7 s^{-1} at 25 °C]. The intermediates in other mechanisms postulated for base hydrolysis are not expected to undergo exchange at significant rates.

We conclude that the decrease in the nitrogen-15 enrichment of the penta-amminecobalt(III) moiety during base hydrolysis, observed in our present experiments, is explicable in terms of simple exchange either of the starting material, $[Co(NH_3)_5Cl]^{2+}$, or of the product, $[Co(NH_3)_5OH]^{+}$. In particular, in the two systems studied here, we have found no evidence for the presence of labile cobalt(II) intermediates.

EXPERIMENTAL

*Measurement of Nitrogen-*15 *Abundance.*—The proton magnetic resonance spectrum of a solution of ammonium sulphate (*ca.* 200 mg) dissolved in 9M-sulphuric acid (*ca.* 0·5 ml) was measured on a Perkin-Elmer R10 spectrometer, with use of increased (×4 or ×8) sensitivity for the peaks due to the less abundant isotope. The percentage abundance of nitrogen-15 is given by $(b \times 100)/(b + af)$, where a is

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* Exchange of $[Co(NH_3)_6]^{3+}$ in aqueous 0·4M-ammonia at 35 °C occurs with half-life = 363 ± 1 days, but the rate was *ca.* three times more rapid during the first few days.[17] Extrapolation of the initial rapid rate to the penta-ammine system (with allowance of a factor of 17 for the combined effect of difference in temperature and ammonia concentration) gives an estimated degree of exchange after 1 h at 23 °C in 14M-ammonia of *ca.* 0·4%.

[15] J. H. Takemoto and M. M. Jones, *J. Inorg. Nuclear Chem.*, 1970, **32**, 175.

[16] D. R. Llewellyn, C. J. O'Connor, and A. L. Odell, *J. Chem. Soc.*, 1964, 196.

[17] A. C. Rutenberg and J. S. Drury, *Inorg. Chem.*, 1963, **2**, 219.

[18] D. R. Stranks, *Discuss. Faraday Soc.*, 1960, **29**, 73.

TABLE 2

Methods for ^{15}N determination

Method	Chemical nature of sample	Size of sample (mg of nitrogen)	Accuracy *	Ref.
Mass spectrometry	Pure dry N_2 gas	0·1—1 mg	±1% standard m.s.	*a*
			±0·1% dual collector m.s.	*b*
			0·01% dual collector m.s. and rapid interchange of sample and standard	*c*
Microwave spectroscopy	NH_3 gas	2 mg	±3%	*d*
Infrared absorption	Pure dry N_2O	6 mg	0·015 atom % at 0·37% abundance	*e*
Emission spectroscopy	N_2 gas	0·01—0·1 mg	1—3% depending on abundance (*f*)	*g, h*
N.m.r.	NH_4^+ salt	2 mg if 20—70% ^{15}N 10 mg if $<5\%$ or $>95\%$ ^{15}N	1—4% depending on abundance	This work

* The errors involved in preparation of samples for ^{15}N analysis have been discussed by J. M. Bremner, H. H. Cheng, and A. P. Edwards, ' Assumptions and Errors in Nitrogen-15 Trace Research,' in ' The Use of Isotopes in Soil Organic Matter Studies,' Special Supplement to the Journal of Applied Radiation and Isotopes, 1966, p. 429.

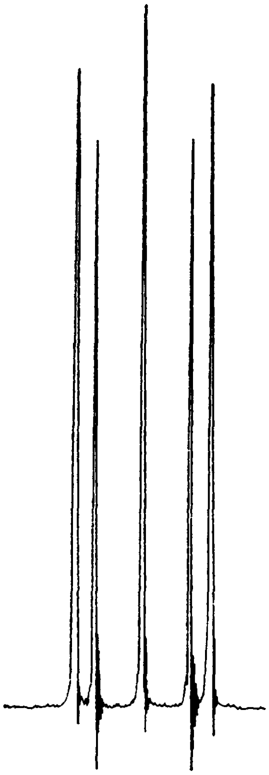
[a] D. Rittenberg, 'The Preparation of Gas Samples for Mass Spectrographic Isotope Analysis,' in ' Preparation and Measurement of Isotopic Tracers,' ed. J. W. Edwards, Ann Arbor, 1947. [b] A. O. Nier, *Rev. Sci. Instr.*, 1947, **18**, 398. [c] C. R. McKinney, J. M. McCrea, S. Epstein, H. A. Allen, and H. C. Urey, *Rev. Sci. Instr.*, 1950, **21**, 724. [d] A. L. Southern, H. W. Morgan, S. W. Keilholtz, and W. V. Smith, *Analyt. Chim.*, 1951, **23**, 1000. [e] J. C. Klyuver, *Rev. Trav. chim.*, 1955, **74**, 322. [f] G. Meier and G. Müller, *Isotopenpraxis*, 1965, **1**, 32. [g] D. Munsche, *Isotopenpraxis*, 1965, **1**, 32. [h] H. Faust, *Isotopenpraxis*, 1967, **3**, 100.

the total height of the three peaks due to $^{14}NH_4^+$, b is the total height of the two peaks due to $^{15}NH_4^+$, corrected if necessary for the sensitivity change of the spectrometer; and f is the correction factor for the extra width of the $^{14}NH_4^+$ peaks (= 1·15 ± 0·03 in this work).

Comments on the Analytical Method.—Methods used to measure the isotopic abundance of ^{15}N are summarised in Table 2. The advantages and disadvantages of all the methods have been discussed by Spindel;[19] the most widely used has been mass spectrometry, although emission spectroscopy is increasingly employed. The proton magnetic resonance spectra of both $^{14}NH_4^+$ and $^{15}NH_4^+$ have been reported;[20,21] in the tetrahedrally symmetric environment of the nitrogen in the $^{14}NH_4^+$ ion, sharp peaks are obtained and quadrupole broadening was apparently not observed. In sulphuric acid solution, proton exchange between NH_4^+ and the solvent does occur,[22] but is so slow that this does not contribute to line broadening. Thus although there has been a considerable amount of work on the detailed n.m.r. spectra (both ^1H and ^{14}N) of [^{14}N]- and [^{15}N]-ammonium salts, it appears previously never to have been applied to isotopic analysis.

The NH_4^+ resonance of ammonium salts in weakly acidic H_2SO_4–H_2O solutions is partly obscured by the large solvent peak. The viscosity of concentrated H_2SO_4 causes broadening of the NH_4^+ resonance. In D_2SO_4 or H_2SO_4–D_2O solutions, ammonium salts undergo slow exchange; the resulting solutions of $[NH_{4-n}D_n]^+$ give incompletely resolved peaks unsuitable for precise measurements. The optimum acid concentration is *ca.* 9M (1 : 1 v/v $H_2SO_4 : H_2O$). Under these conditions a standard solution of $(NH_4)_2SO_4$ (18 mg in 0·3 ml; 32% ^{15}N by mass spectrometry) shows completely separated spectra of $^{15}NH_4^+$ and $^{14}NH_4^+$ (see Figure). Integration of the $^{15}NH_4^+$ doublet and the $^{14}NH_4^+$ triplet gave values of 31·63 ± 0·49 and 31·64 ± 0·66% ^{15}N (measured on Perkin-Elmer R10 and Jeol PS100 spectrometers respectively). This method can be used satisfactorily for samples containing 25—60% ^{15}N, but it is not feasible to integrate weak and strong peaks in close proximity for enrichments outside these limits.

Calculation of the ^{15}N abundance of the 32% standard sample directly from the peak heights (measured a large number of times) gave values of 34·62 ± 0·60% ^{15}N (Perkin-Elmer R10) and 36·14 ± 0·62% ^{15}N (Jeol PS100).



^1H N.m.r. spectrum of $(NH_4)_2SO_4$ containing 32% nitrogen-15

Comparison of the results obtained using the two spectrometers reveals a difference in the relative line-widths of the $^{14}NH_4^+$ and $^{15}NH_4^+$ peaks. As measured on the Perkin-Elmer R10 spectrometer, the former were consistently 15 ± 3% broader than the latter (mean of values obtained during a two-year period) and the difference did not seem to

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[19] W. Spindel, ' Nitrogen-15,' in ' Inorganic Isotopic Syntheses,' ed. R. H. Herber, Benjamin, New York, 1962, especially pp. 79—87.

[20] R. A. Ogg, *Discuss. Faraday Soc.*, 1954, **17**, 215.

[21] G. Binsch, J. B. Lambert, B. W. Roberts, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1964, **86**, 5564.

[22] R. B. Johannesen, *J. Chem. Phys.*, 1968, **48**, 1414.

depend on the degree of tuning or the homogeneity of the spectrometer magnetic field. A different relative line-width was obtained for the Jeol PS100 instrument and it is clearly necessary to determine this parameter for each spectrometer (preferably by use of a sample containing 30—40% ^{15}N). The ^{15}N concentrations in samples of ammonium sulphate (of natural isotopic abundance, and of 96 and 99% enrichment) were determined from the peak heights and corrected for the different line-widths: 0·357 ± 0·017, 96·32 ± 0·13, and 99·22 ± 0·20% (Perkin-Elmer R10 spectrometer with 4× or 8× increased sensitivity for the peaks due to the less abundant isotope). Satisfactory results were also obtained with the Jeol PS100 spectrometer with a sensitivity change of 10× for the weaker peaks.

In addition to direct determination of ^{15}N in ammonium salts dissolved in 50% v/v sulphuric acid, analyses have been carried out on a number of organic nitrogen-containing compounds after first subjecting them to Kjeldahl degradation on a microscale. Oxidation of material containing 3—5 mg nitrogen * with 0·5—1·0 ml AnalaR sulphuric acid gave a solution suitable for the n.m.r. determination, after transfer of the acidic ammonium sulphate solution to the n.m.r. tube with water (0·2 ml) (some sulphuric acid is distilled off during this small-scale Kjeldahl digestion, so the volume of the resulting solution for n.m.r. is 0·4—0·6 ml). Some catalysts conventionally used for the Kjeldahl digestion are unsuitable, especially copper(II) sulphate whose paramagnetism causes excessive line-broadening of the n.m.r. resonances. However potassium sulphate can advantageously be added to accelerate the digestion by increasing the reaction temperature. In cases of difficulty brown carbonaceous materials, present in the final stages of the digestion, can be destroyed by the addition of a very small amount of AnalaR concentrated perchloric acid (there is no detectable loss of sensitivity due to oxidation of the ammonia). The perchloric acid is then evaporated off before the n.m.r. determination. [^{15}N]-labelled compounds including glycine, alanine, phenylalanine, glutamic acid, phthalimide, urea, ethylenediamine, and acetamide were treated in this way and all gave values for the abundance of ^{15}N in good agreement with those for the ammonium salts used in their syntheses.

Inorganic compounds which after Kjeldahl degradation yield paramagnetic metal ions [*e.g.*, cobalt(III) complexes which give paramagnetic cobalt(II)] must be decomposed in a different manner, *e.g.*, by heating with an excess of alkali and distilling the ammonia into acid. This can be done in the normal apparatus for distillation of ammonia after a micro-Kjeldahl digestion. This is the method of decomposition used in the analysis of the metal complexes discussed in this work.

Of all the methods now available for determination of ^{15}N abundance, by far the most accurate is mass spectrometry which, furthermore, requires only a small sample. However, contamination with natural-abundance nitrogen can be a problem; if this arises from atmospheric nitrogen a correction can be applied but may lead [19] to considerable loss of accuracy. Moreover for work of high precision a mass spectrometer must be used solely for ^{15}N analysis (in order to obtain low ^{14}N blanks). A vacuum line is essential for preparation of samples for mass spectrometric determination and for analysis by emission spectroscopy. The latter method requires a special piece of equipment, which can be used only for ^{15}N analysis. Our results show that the ^{15}N abundance of a wide range of compounds may readily be determined on a small sample, after Kjeldahl degradation, by using the ^{1}H n.m.r. method described in this paper. Although greater accuracy or smaller sample size can be obtained with the other methods, these disadvantages are outweighed by the ease of determination and the absence of need to reserve specialized apparatus for this one purpose.

Materials.—[^{15}N]Ammonium sulphate (30 and 99·1% enrichment) was purchased from Prochem Ltd. and the isotopic composition checked before use.

Chloropenta-amminecobalt(III) chloride. Samples containing natural-abundance ^{15}N were prepared by the literature method.[23] The following modified procedure was adopted for ^{15}N-enriched complex. [^{15}N]Ammonium sulphate (4·00 g, 99·1% ^{15}N) in water (25 ml) was treated with potassium hydroxide (9 g). The liberated gaseous [^{15}N]ammonia was passed through a drying tube containing potassium hydroxide and through an acetone–solid carbon dioxide trap before collection in a liquid-nitrogen trap (yield determined by measurement of the pressure in a calibrated volume was 59·7 mmol, 81·4%). The ammonia was distilled into an evacuated reaction flask containing cobalt(II) chloride hexahydrate (1·045 g) and hydrochloric acid (5 ml, 4N). The mixture was allowed to warm to room temperature and, while being stirred continuously, hydrogen peroxide (1 ml, 30%) and then concentrated hydrochloric acid (3 ml) were slowly added. The reaction vessel was removed from the vacuum line and heated on a water-bath for 15 min. On cooling, the product crystallized and was collected, washed with 6N-hydrochloric acid, with methylated spirit, and with acetone, and dried at 110 °C (yield 0·805 g). (Found for natural-abundance complex: H, 6·1; N, 27·9. Calc. for $H_{15}Cl_3CoN_5$: H, 6·0; N, 27·9 Found for [^{15}N]-complex: H, 6·0; ^{15}N, 28·6%. Calc. for $H_{17}Cl_3Co^{15}N_5O$: H, 5·8; ^{15}N, 29·0%).

Acetatopenta-amminecobalt(III) nitrate was prepared from carbonatopenta-amminecobalt(III) nitrate by the literature method [24] (yield 58%) (Found: C, 6·9; H, 5·7; N, 29·3. Calc. for $C_2H_{20}CoN_7O_9$: C, 7·0; H, 5·8; N, 28·4%).

Base Hydrolysis of Natural-isotopic-abundance Complexes in the Presence of [30% ^{15}N]*Ammonia*.—A solution of chloropenta-amminecobalt(III) chloride (0·19 g, 0·74 mmol) and [30% ^{15}N]ammonium sulphate (0·5 g, 3·78 mmol) in water (50 ml) was treated with sodium hydroxide solution (1N, 9 ml). After *ca.* 30 min at *ca.* 23 °C, the uncomplexed ammonia and most of the water were removed by evacuation of the reaction flask. When the volume of liquid remaining in the flask had fallen to 5 ml, further water (10 ml) was added and the mixture evacuated to dryness. The red solid complex was decomposed with excess of sodium hydroxide and the liberated ammonia and water were collected in a liquid-nitrogen trap containing sulphuric acid (4N, 3 ml). The trap was allowed to warm up to room temperature and the water removed under vacuum, with gentle heating. The residual solid ammonium sulphate was dissolved in sulphuric acid (6M, 0·5 ml) and analysed for ^{15}N.

Acetatopenta-amminecobalt(III) nitrate (0·211 g, 0·63 mmol) and [30% ^{15}N]ammonium sulphate (0·50 g, 3·78 mmol) in water (70 ml) were treated with sodium hydroxide

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* For samples containing 5—95% enriched ^{15}N, 5 mg is sufficient; less is required for 20—70% ^{15}N and correspondingly more for very high or very low enrichments.

[23] G. G. Schlessinger, *Inorg. Synth.*, 1967, **9**, 160.

[24] F. Basolo, J. G. Bergmann, and R. G. Pearson, *J. Phys. Chem.*, 1952, **56**, 22.

(1N, 9 ml) at 0 °C for 1 h. The product was separated and the co-ordinated ammonia converted into ammonium sulphate as described above.

Base Hydrolysis of $[Co^{15}NH_3)_5Cl]^{2+}$ *in Concentrated Ammonia Solution of Natural Isotopic Abundance.*—$[Co^{15}NH_3)_5Cl]Cl_2$ (0·18 g, 0·7 mmol) was dissolved in concentrated ammonia solution (75 ml, *d* 0·88 g cm^{-3}) and stirred at *ca.* 23 °C for 45 min. Then the free ammonia in solution and most of the water were removed under vacuum. Sodium hydroxide solution (7 ml, 0·1N, 0·7 mmol) was added to decompose the ammonium chloride formed as a by-product during the hydrolysis. The volume of solution was reduced to *ca.* 2 ml by evacuation, during which time a very small amount of the cobalt complex decomposed to give brown solid. The solution was chromatographed on cation exchange SP Sephadex C-25 eluting with an aqueous solution buffered at pH 9·2 (0·5M-sodium chloride and 0·01M borax). In order of elution the following fractions were obtained: (1) a faint purple band of unchanged $[Co(NH_3)_5Cl]^{2+}$ (some or all of this may not be unchanged factor, but may have been formed by partial reversal of base hydrolysis during the chromatography); (2) a main red band of $[Co(NH_3)_5OH]^{2+}$; (3) a slowly moving yellow band of $[Co(NH_3)_6]^{3+}$; and (4) traces of dark brown decomposition products adhering to the top of the column. The red fraction was treated with sodium hydroxide (1 g) and the ammonia and water were removed under vacuum and collected in a trap containing sulphuric acid (4N, 3 ml) cooled by liquid nitrogen. The volume of the warmed solution was reduced to *ca.* 0·3 ml and analysed for ^{15}N. Care was required during the destruction of complex to ensure that no solid was carried over into the collecting vessel [paramagnetic impurities such as cobalt(II) cause unacceptable broadening of the ^{1}H n.m.r. peaks] and an anti-splash head and efficient glass wool plugs were found necessary. In one experiment the $[Co(NH_3)_6]^{3+}$ produced during the reaction was decomposed by addition of KOH and the ammonia produced distilled into an excess of dilute sulphuric acid; the volume of the resultant ammonium sulphate solution was reduced to *ca.* 0·5 ml and analysed for ^{15}N.

A sample of unchanged $[Co(^{15}NH_3)_5Cl]Cl_2$ (0·1467 g) was decomposed with sodium hydroxide solution (1 g/*ca.* 15 ml H_2O) and the liberated ammonia was collected as described above and analysed for ^{15}N.

Control Experiments.—The changes in the electronic spectrum showed that the reaction of the complexes in basic solution followed the expected course. Moreover the soluble products from reaction of $[Co(NH_3)_5Cl]Cl_2$ in concentrated aqueous ammonia (30 min, *ca.* 23 °C) were separated on SP Sephadex C-25 (see above) and shown to be $[Co(NH_3)_5OH]^{2+}$ (83%), $[Co(NH_3)_6]^{3+}$ (12%), and $[Co(NH_3)_5Cl]^{2+}$ (5%).

All the reactions used in the hydrolysis, chromatographic separation, or work-up procedure were tested for contamination with ammonia by use of Nessler's reagent and subsequent spectrophotometric analysis[25] at 425 nm. No ammonia was found and, since the detection limit is 0·5 μg NH_3/ml, the upper limit for extraneous ammonia introduced into the n.m.r. tubes in this way is less than 0·1% of the total sample.

We confirmed that our procedure for removing uncomplexed ammonia from a solution was satisfactory. Concentrated ammonia solution (75 ml) was treated with aqueous sodium hydroxide (5 ml, 0·1N) and the volume reduced to 2 ml by evacuation; water (15 ml) was added and the volume again reduced to 2 ml; no residual ammonia was detected with Nessler's solution. Further, no ammonia was detected in the solution eluted between the fractions containing cobalt(III) complexes in a chromatographic separation of the products of base hydrolysis of $[Co(NH_3)_5Cl]Cl_2$ in concentrated aqueous ammonia after application of our work-up procedure.

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[25] A. I. Vogel, ' Quantitative Inorganic Analysis,' 2nd edn. Longmans, London, 1957, p. 783.