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CARBONATO COMPLEXES OF COBALT(III)

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CONTENTS

For abbreviations see p. 198.

A. INTRODUCTION

This review of the carbonato ammino derivatives of cobalt(III) covers the subject exhaustively until 1968 and includes our own experience and comment. Special attention is paid to the carbonato pentammine and carbonato tetrammine series since considerable effort has been expended thereon.

B. PREPARATION AND CRITERIA OF PURITY

The preparation of $[Co(NH_3)_5CO_3]X$, $[Co(NH_3)_4CO_3]X$ and $[Co(CO_3)_3]M_3$ is accomplished by oxidation of $[Co(H_2O)_6]^{2+}$ in the presence of convenient reactants.

The pentammino and tetrammino compounds are satisfactorily obtained using ammonia and ammonium carbonate as reactants and air (oxygen) or H_2O_2 as oxidant.

There are other less important methods of formation such as degradation of hexammines in acid aqueous solution; regulated heating of solids (hexammines) or using bicarbonato derivatives as starting material.

A general method for cobaltammines[28] using $K_3[Co(CO_3)_3]$ (ref. 21), $Na_3[Co(CO_3)_3]$(ref. 27) or the "Green Field-Durrant Solution" is of some interest.

The $[Co(NH_3)_4CO_3]^+$ compounds[30–34,36,37] may be obtained by Jørgensen's original method[35].

Jørgensen's method is included in almost every inorganic preparations manual, *e.g.*: E. G. Biltz, Walton, King, Grubitsch, Duval, etc. A tested technique by Shoelessinger is included in Inorganic Syntheses Vol. VI. The use of H_2O_2 as an oxidant is presented as an alternative. The method can be used for several salts changing the cobalt salt used as starting material.

The transformation of nitrate to chloride has been reported by using ion exchange resins[29,47].

In the case of $[Co(NH_3)_4CO_3]Cl$, Lamb and Damon[38] observed a low and variable chloride content, and a modified preparative method was proposed.

The Lamb and Damon method has seldom been employed[39].

The carbonato pentammino derivatives, $[Co(NH_3)_5CO_3]X$, were first obtained by Vortman and Blasberg but they considered them as dinuclear compounds, $[Co_2(NH_3)_{10}(CO_3)_2]^{2+}$, probably due to their reluctance to accept the monodentate CO_3^{2-} coordination. Werner and Gosling[40] and Werner[41] indicated the correctness of the pentammino formula $[Co(NH_3)_5CO_3]X$ for these compounds. Nitrate, bromide and iodide derivatives were prepared but difficulties were observed in the preparation of the chloride and oxalate. Kranig[26,42] was able to prepare both compounds; he also modified the Werner method for bromide and iodide.

The modified Werner method is included in Inorganic Syntheses Vol. IV. It is necessary to recrystallize the first crop due to the presence therein of rose-cobaltic contamination. The method consists essentially in the air oxidation of $[Co(H_2O)_6]^{2+}$ mixed with ammonium carbonate and ammonia. Afterwards the red solution is kept overnight near 0° for crystallization.

The original method was also studied by Briggs[43] who proposed some changes.

The Briggs method, sometimes with slight modification, has been used quite generally in various researches cited in this review[31,33,44–46], although since publication (in Inorganic Syntheses) of the Basolo and Murmann modification, the easy availability of this guaranteed technique has altered the situation.

The preparation of $[Co(NH_3)_5CO_3]X$ and $[Co(NH_3)_4CO_3]X$ differs in two aspects: concentration of the reactants and crystallization conditions. When a water solution of $[Co(NH_3)_5CO_3]NO_3$ is concentrated by heating and $(NH_4)_2CO_3$ is added as in the preparation of $[Co(NH_3)_4CO_3]X$, crystallization yields the tetrammino derivative. On the other hand, when the tetrammino derivative is inversely treated there is no transformation.

These experiments support the logical idea that concentration of the reactants controls the preferential formation of each salt and also that crystallization by steam bath evaporation or cooling the concentrated solution is a fundamental determining factor in these methods.

The solubility of $[Co(NH_3)_5CO_3]X$ at low temperature has been reported to be small[31]. If the solution used in the formation of the tetrammino derivative contains some pentammino derivative, evaporation and addition of $(NH_4)_2CO_3$ should produce the pure tetrammine.

Criteria of purity

The purity of carbonato-ammino Co^{III} complexes is checked in the same general way as that of all Co^{III} ammino complexes. Quantitative analysis is generally used but the coincidence of experimental and calculated analysis does not mean absolute purity. The nature of the impurities usually present, (generally other similar complexes) reduces the meaning of matching figures. The simultaneous control of several components, *e.g.*: Co, NH_3, H_2O, builds up much better confidence in this analytical match type of control.

These well known problems in coordination chemistry led to a search for better criteria of purity. The quantitative verification of visible spectra when well known, has been proposed by Nakamoto and co-workers and in some cases it is a unique and sufficient criterion of purity.

Experience shows that the quantitative analysis of various components together with spectral verification, (or some other measurable property, such as conductivity) are the best practical criteria of purity for cobalt ammines.

We will briefly consider some of the analytical methods which are best fitted for control purposes. The spectra check will be covered later on (see p. 174).

Co % determination

Some of the following gravimetric methods can be useful:

Sulfate conversion.—Almost every cobaltammine converts to $CoSO_4$ when conveniently treated with sulfuric acid. The accuracy of the method can be very good. The assay sample is usually kept in the same crucible during all manipulations. If previous decomposition of the complex, using sulfide or hydroxide precipitation, is needed, the simplicity is lost.

This method demands experience and is time consuming, and even in expert hands the chances of failure are many. However, in practice it is the most frequently used method.

Electrogravimetric method.—This method for determination of cobalt is included in most Analytical Chemistry treatises, and involves weighing electrolytically deposited cobalt metal.

In spite of this procedure's simplicity and apparent trouble-free characteristics it has not been widely used[48] so far for the purity control of cobalt ammines. The analytical results from such a method indicate no better than 0.5% reproducibility. However by employing a modification reported by Siebert[49] reproducibility can be better than 0.1%.

In some cases, such as with insoluble compounds or very stable complexes, a prior decomposition step must be included; we have used a Kjeldhal type of sulfuric acid attack.

Conversion to cobalt oxide and hydrogen reduction.—This is the best method[50,51] when the compound can be directly destroyed to Co_3O_4. Reproducibility is 0.01%.

Ammonia

Ammonia is most conveniently analysed by the method of Horan and Eppig[53].

Carbonate

Two methods are employed; $BaCO_3$ precipitation after aquation[31] and CO_2 liberation and absorption[32] in standard $Ba(OH)_2$.

Anionic complexes derived from $[Co(CO_3)_3]^{3-}$ are important as starting materials for the syntheses of many cobalt^{III} complexes. Most of the typical examples occur in the group of compounds we are reviewing.

In 1862, Field[55] discovered that oxidation of cobalt in bicarbonate solution produces green colors. The oxidation agents were H_2O_2 or hypochlorites.

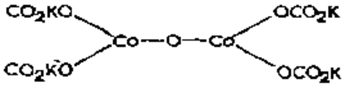
A. Job[56,57] describes the phenomenon in a more detailed way. When a cobalt salt solution is slowly added to concentrated $KHCO_3$ solution a rose precipitate is formed which redissolves on stirring, giving a deep violet liquid. On adding H_2O_2 or Cl_2 it quickly turns to a very deep green. The formation of this color is a very sensitive and characteristic test for cobalt.

Job's studies showed the tripositive valence state of the metal and his analytical work gave the formulation $Co_2O_32CO_2$.

Durrant[58] reported that several anions, such as oxalates, tartrates and citrates also produce green colored solutions in similar reactions. The oxalato derivative was isolated as a solid, and studied. For the carbonato reactions he suggested the following interpretation:

$$4KHCO_3+2CoCO_3+H_2O_2 = [Co(KCO_3)_2]_2O+2CO_2+3H_2O$$

and the formula for the product:



The common green color was attributed to the ($>$Co–O–Co$<$)-carboxylic bonds.

Kranig[26,59] described trioxalate derivatives of formula $K_3[Co(C_2O_4)_3]3H_2O$. Bernard and Job[60] reported spectrophotometric data on the green carbonato solution but did not resolve any structural points. C. Duval[61] obtained $Co[Co(CO_3)_3]$ supporting the formula adopted with analysis, stoichiometric iodine liberation, electrophoresis and analogies.

After that, analytical interest in such green solutions was intensified. In 1951 Laitinen and Bundett[62] reported a method using the green solution as an oxidant combined with iodometric titration. Ayres[63] developed a colorimetric method for the determination of cobalt. Telep and Bolty[64] reported a spectrophotometric method for cobalt based on the use of the 260 mμ maximum which follows Beer's law.

The use of the oxidation power of Co^{III} bicarbonato solutions as a titration solution offers interesting analytical possibilities but is handicapped by the great instability of the solutions.

Baur and Bricken[65] reported using anhydrous $[Co(NH_3)_6][Co(CO_3)_3]$ which is stable in dry air. The bicarbonato solutions of this compound are much more stable. (Their concentration is reduced to half saturation in 3 months). The solubility is only 0.038 g in 100 g of water[21] but the compound can be used according to the method given. This compound $[Co(NH_3)_6][Co(CO_3)_3]$ was first obtained by McCutcheon and Schuele[66] and its anhydrous character is of some importance, as will be seen. The compound is prepared by using $[Co(NH_3)_4CO_3]_2SO_4$, $KHCO_3$ and $K_2S_2O_8$, and adding $[Co(NH_3)_6]^{3+}$ as a precipitant.

The first alkali metal salt isolated was reported by Mori, Shibata, Kyuno and Adachi[21] who prepared $K_3[Co(CO_3)_3]3H_2O$. The formula was based on analysis and absorption spectra. Light, humidity and a little rise in temperature decompose the salt. It decomposes on standing.

Bauer and Drinkard[27] suggested the use of the sodium salt, $Na_3[Co(CO_3)_3]\cdot 3H_2O$, which is insoluble and much more stable, inasmuch as it is possible to keep it a long time in a dark and dry place. The preparation of $Na_3[Co(CO_3)_3]3H_2O$, and its applications are reported in Inorganic Syntheses, (V. 8, 1966).

The use of $[Co(CO_3)_3]^{3-}$ as a starting material for other preparations does not necessarily depend on any of the above cited solids. It is safer and more practical to start directly from freshly prepared Field Durrant Solution[14,19,23,24] and no analytical control is necessary.

Three comprehensive reviews[16,28,67] have been written by M. Shibata, head of the Japanese group, dealing with their work on the syntheses of several compounds from $[Co(CO_3)_3]^{3-}$.

C. AQUEOUS SOLUTION EQUILIBRIA

(i) *Mechanisms of acid-hydrolysis. Kinetics, $^{14}CO_3{}^{2-}$ exchange, ^{18}O tracer and polarographic studies*

The behaviour of $[Co(NH_3)_5CO_3]^+$ and $[Co(NH_3)_4CO_3]^+$ in aqueous solution has been studied since the beginning of Coordination Chemistry, and has produced an impressive number of papers. Through this type of study importance knowledge of the bonding of the $CO_3{}^{2-}$ group has been gained.

Aqueous solutions of $[Co(NH_3)_5CO_3]^+$ and $[Co(NH_3)_4CO_3]^+$ hydrolytically decompose quite rapidly. A solution of $[Co(NH_3)_4CO_3]NO_3 \cdot 0.5H_2O$ becomes turbid; this turbidity is photometrically detectable in a few minutes, (10 min. at 25°). The $[Co(NH_3)_5CO_3]NO_3H_2O$ solution remains unchanged.

Kranig observed[59] that since Werner's time it was known that tetrammines and pentammines undergo hydrolysis resulting in a change in conductivity. The carbonato derivatives shows these changes although the experimental values of the molar conductance stay within the limits for univalent salts, for long enough to make meaningful measurements. The color changes are easily detected and it follows that to record properly the solution spectra of these complexes some kind of stabilization must be used.

Dahr[68] reported that total decomposition of $[Co(NH_3)_4]NO_3aq$ takes place in 20 hours at 30°. The hydrolytic process produces precipitation.

On adding small quantities of acid the process is altered. Jørgensen[69] reported that in 1M acid solution the $[Co(NH_3)_4CO_3]^+$ ion is transformed into the di-aquotetrammine. This reaction is now called acid hydrolysis or aquation.

$[Co(NH_3)_4CO_3]^+ + 2H^+ + 2H_2O \rightarrow [Co(NH_3)_4(H_2O)_2]^{3+} + H_2CO_3$. If the acid concentration is higher, aquo-acido and diacido species can be produced.

$$[Co(NH)_4CO_3]^+ + 2HX + H_2O \rightarrow [Co(NH_3)_4XH_2O]^{2+} + X^- + H_2CO_3$$
$$[Co(NH_3)_4CO_3]^+ + 2HX \rightarrow [Co(NH_3)_4X_2]^+ + H_2CO_3.$$

The decomposition equilibria for H_2CO_3, should be considered.

These processes have been studied through changes in conductance, pH, color, and CO_2 evolution.

Uspenski and Tschibishoff[70] followed the transformation of $[Co(NH_3)_4CO_3]^+$ by pH measurements and color changes.

Pedersen[30] investigated the kinetics using CO_2 pressure measurements. The experimental data can be fitted partially by a two term law, one independent and the other directly proportional to $[H^+]$.

Four series of experiments were presented with varying total concentration in glycocolate buffer and acetate buffer, (Temp. 25°).

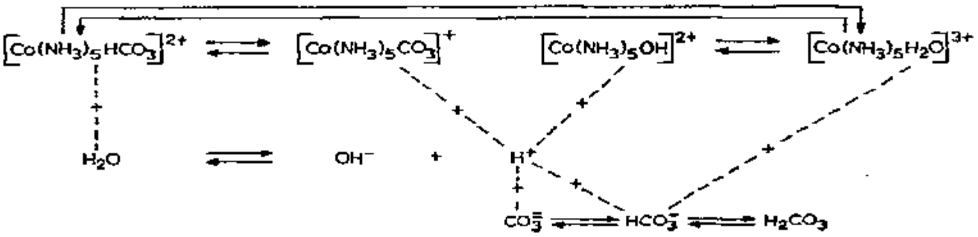
The half decomposition time at 25° varies among different runs between 160 and 20 minutes the resultant equation is only good for small pCO_2 and high $[H^+]$ values. This report was purely experimental and the selection of a rate law was empirical. No mechanistic considerations were presented.

Y. Wormser[71], in a general study of the reactions of substituted ammino complexes, found that in every case the transformation involves the intermediate formation of an aquocomplex, *viz.*

$$CoA_4L_2 \xrightarrow{H_2O} CoA_4LH_2O \xrightarrow{H_2O} CoA_4(H_2O)_2$$

This applied to the $[Co(NH_3)_4CO_3]^+$ species as well. This type of intermediate compound was first suggested by Mathieu[72] for the aquation of $[Co(en)_2Cl_2]^+$. On the basis of this work, the mechanism of Co^{III} carbonato ammino complexes aquation was eventually deduced.

The ionization and aquation equilibria produce several interdependent ionic equilibria as follows:



The first and one of the most important reports was from Lamb and Mysels[31] on $[Co(NH_3)_5CO_3]^+$. They discuss, the ionic interdependent equilibria and present the kinetics of the aquation through conductometric and potentiometric measurements. A complete interpretation of the aquation phenomena emerges quantitatively. The following equilibrium constants were reported:

$$\frac{[Co(NH_3)_5OH^{2+}]\,[HCO_3^{\,-}]}{[Co(NH_3)_5HCO_3^{\,2+}]} = C = 8.5 \times 10^{-4}$$

$$\frac{[Co(NH_3)_5HCO_3^{\,2+}]}{[Co(NH_3)_5CO_3^{\,+}]\,[H^+]} = K = 4 \times 10^{-7}$$

These values indicate that the bicarbonato pentammino Co^{III} concentration will equal the carbonato pentammino Co^{III} conc. when $[H^+] = 4 \times 10^{-7}$, corresponding to pH = 6.5.

For the kinetic study they define two parameters:

$$\text{aquation degree, } a = \frac{\text{aquated ammine}}{\text{total ammine}} = \frac{\text{uncomplexed } CO_2}{\text{total } CO_2}$$

which they relate to the quantities of ideally total aquated complex and non-aquated to define any state of the system.

$$\text{neutralization degree, } b = \frac{\text{strong acid added}}{\text{complex added}}$$

Both parameters can be experimentally determined and also calculated from the equilibrium constants. The agreement between calculated and experimental values is considered a good test of the correctness of the interpretation.

In order to follow the aquation process by electrometric measurements, the rate of aquation has to be slow enough vis a vis the ionization equilibrium setting.

Previous experimental work[99] indicated that 0.003M sol. of $[Co(NH_3)_5HCO_3]^{2+}$ at 0° aquates totally in 20 minutes whilst $[Co(NH_3)_5CO_3]^+$ needs several hours under the same conditions. At 25° both processes are speeded up.

Bearing this in mind, Lamb and Mysels made conductometric measurements of the aquation process. The measurements were obtained by previous adjustment of the bridge to some value and finding the time for balance.

The aquation behaved as a unimolecular reaction.

The rate constant values at 25° are:

conc. mol/lt.	k_1+k_2 min^{-1}
0.02	0.070
0.004	0.095
0.001	0.218

At 0° with $\frac{1}{2}$ and $\frac{3}{4}$ equivalent HCl added they obtained 0.109 and 0.122 min^{-1} respectively.

The rate constant variation with added acid shows a linear dependence. The initial pH was not measured because of the speed of the reaction, but its time variation was tabulated and plotted. A complex solution with added acid implies a certain degree of neutralization and the variation of pH from this initial state is determined.

Experiments of this type are reported for 0° and 25°, and show that aquation is completed in 30 minutes to 1 hour.

For $[Co(NH_3)_5HCO_3]^+$ a somewhat higher rate was found. In a general discussion of the results the authors concluded that in the aquation of $[Co(NH_3)_5CO_3]^+$ $\frac{1}{8}$ of the reaction proceeds via the intermediate formation of the bicarbonate species, whilst $\frac{7}{8}$ proceeds directly. This conclusion however rests on tenuous evidence.

Two side aspects are considered in this report[31]. One of them refers to conductometric work done by Duff[100] who attributed a catalytic effect due to the platinum electrodes and the other to the effect of light on the aquation process, claimed by Schwartz and Tede[101].

Lamb and Mysels found that the catalytic effect is real but small, if the electrodes are kept for long periods of time in the ammines solutions. The effect of light is stated as non-existent.

Thereafter studies of the aquation of carbonato-ammino Co^{III} complexes developed through radiochemistry techniques using $^{14}CO_3{}^{2-}$ and ^{18}O tracers. This type of work yielded detailed information about the aquation process and linkage of the $CO_3{}^{2-}$ group.

In 1950 G. M. Harris[102] discovered the exchange between

$[Co(NH_3)_4CO_3]NO_3$

and ^{14}C labelled Na_2CO_3. A 0.03M complex solution, mixed with 0.01M Na_2CO_3 containing ^{14}C, shows isotopic exchange, $T_{\frac{1}{2}} = 7$ hrs. in the dark at 20°. The reaction is 1st order.

Evidently, the study of these phenomena show promise, particularly iu order to gain deeper insight into the mechanism of $CO_3{}^{2-}$ entering and leaving the complex matrix, and of the differences and similarities between the various species.

A kinetic study of the exchange with $[Co(NH_3)_4CO_3]^+$ was published[32] in 1952. Isotopic effect, hydrogen concentration, ionic strength and temperature variations vis a vis $T_{\frac{1}{2}}$ are presented. The following mechanism is proposed:

$$[Co(NH_3)_4CO_3]^+ + H_3O^+ \rightleftarrows [Co(NH_3)_4HCO_3 \cdot H_2O]^{2+} \qquad (1)$$

$$[Co(NH_3)_4HCO_3H_2O]^{2+} + H^{14}CO_3{}^- \rightleftarrows$$
$$\rightleftarrows [Co(NH_3)_4H^{14}CO_3 \cdot H_2O]^{2+} + HCO_3{}^- \qquad (2)$$

$$[Co(NH_3)_4HCO_3H_2O]^{2+} + H_2O \rightleftarrows [Co(NH_3)_4(H_2O)_2]^{3+} + HCO_3{}^- \qquad (3)$$

$$[Co(NH_3)_4(H_2O)_2]^{3+} + H^{14}CO_3{}^- \rightleftarrows [Co(NH_3)_4H^{14}CO_3H_2O]^{2+} + H_2O \qquad (4)$$

$$[Co(NH_3)_4H^{14}CO_3H_2O]^{2+} \rightleftarrows [Co(NH_3)_4{}^{14}CO_3]^+ + H_3O^+ \qquad (5)$$

Taking into account the facts that reactions 1 and 5 are fast in comparison with 2, 3 and 4, that the diaquotetrammine Co^{III} concentration is small and can be considered invariable during the process and some other simplifications, the authors develop an expression for $T_{\frac{1}{2}}$ as a function of known constants and some measurable concentrations. The rate of exchange calculated for a mechanism consisting in simultaneous (1,2,5) and (1,3,4,5) paths reproduces the experimental function. Path (1,2,5) is the principal one and the total aquation (3) plays only a small part in the process. As a consequence the exchange proceeds mainly by:

1) aquation and protonation with ring opening.
2) Interchange of $H^{14}CO_3$ with HCO_3
3) deprotonation of the labelled intermediate with ring formation.

The experiments cover concentrations from 0.005M to 0.1M of complex and from 0.00765 to 0.03662M of total carbonate. The accepted aquation mechanism is:

$$[Co(NH_3)_4CO_3]^+ + H_3O^+ \rightarrow [Co(NH_3)_4HCO_3H_2O]^{2+}$$
$$[Co(NH_3)_4HCO_3H_2O]^{2+} + H_3O^+ \rightarrow [Co(NH_3)_4(H_2O)_2]^{3+} + H_2CO_3$$

in accordance with established ideas.

An aquation step prior to interchange appears to be necessary in order to understand the rate of interchange. The reactivity of the bidentate CO_3 group in solution is also explained on the basis of aquation followed by ring opening.

The same authors[105] reported a more intensive study of the isotopic effect cited above. The experiment was planned to probe the interchange equilibria and acid decomposition of $[Co(NH_3)_4CO_3]^+$ both normal and labelled.

The experimental equilibrium constant

$$K = \frac{[Co(NH_3)_4{}^{14}CO_3{}^+][HCO_3{}^- + CO_3{}^{2-}]}{[Co(NH_3)_4CO_3{}^+][H^{14}CO_3{}^- + {}^{14}CO_3{}^{2-}]}$$

directly measures the isotopic enrichment in the complex corresponding to the ratio of specific activity in the complex in equilibrium, with the specific activity in the uncomplexed carbonate ions.

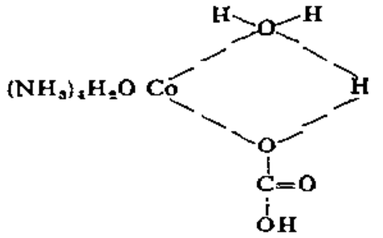
They found $K = 0.89$ at 25° and 0.875 at 0°, (pH 9.7, conc. complex 0.03 to 0.06M, conc $CO_3{}^{2-}$ 0.015M). These values imply a considerable and unexpected isotopic effect.

Harris and Stranks explaned this isotopic effect as follows: the carbonato group through chelation loses its symmetric XY_3 structure becoming XYZ_2, the O–C bonds being weakened by Co linkage. The effective mass of these oxygen atoms becomes bigger, thus accounting for the isotopic discrimination. In saying so, the authors mention that the structure of $[Co(NH_3)_4CO_3]^+$ is not known in sufficient detail to permit a direct determination of the partition function. This interpretation has, of course, a qualitative character. Since the absolute structure of the ion is now known these calculations should be performed.

Regarding acid decomposition, experiments are in accord with the following mechanism:

$$[Co(NH_3)_4CO_3]^+ + H_3O^+ \rightarrow [Co(NH_3)_4HCO_3H_2O]^{2+} \textit{ rapid}$$
$$[Co(NH_3)_4HCO_3H_2O]^{2+} + H_3O^+ \rightarrow$$
$$\rightarrow [Co(NH_3)_4(H_2O)_2]^{3+} + H_2O + CO_2 \textit{ slow}$$

The second reaction determines the total velocity of the process. The activated complex suggested for this second reaction is



A short time afterwards, Stranks[136] considered the relative incidence of aquation as well as the direct interchange mechanism and showed that there is a dependence on the carbonate ion concentration. The aquation mechanism takes care of almost the whole reaction only when the solution is dilute. At higher concentrations the direct mechanism increases in importance. This direct interchange mechanism which functions in concentrated carbonato solutions is:

$$[Co(NH_3)_4CO_3]^+ + {}^{14}CO_3{}^{2-} \rightarrow [Co(NH_3)_4{}^{14}CO_3)^+ + CO_3^{2-}$$

The results indicated 65.9% direct mechanism and 34.1% aquation mechanism under concentrated conditions, but only 0.6% direct and 99.4% aquation for diluted solution.

Jankwich and McNamara[103] using ^{13}C and ^{14}C studied the exchange with $[Co(en)_2CO_3]^+$. The ^{13}C distribution was measured by mass spectroscopy and the ^{14}C by using an electrometer. The interchange constants were:

$0.99 \pm 0.01_4$ for ^{13}C

and

$0.99 \pm 0.01_2$ for ^{14}C

This complex, although very similar to $[Co(NH_3)_4CO_3]^+$ behaves differently: it does not exhibit an isotopic effect.

The authors relate the difference in lability of $CO_3{}^{2-}$ ligand to the sharing of coordination sites either with four ammonia or two ethylenediamine groups, in order to explain the observed isotopic effect of $[Co(NH_3)_4CO_3]^+$.

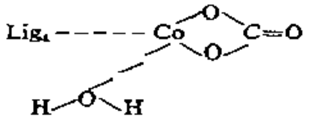
The results were verified by Stranks[104] who also worked with $[Co(NH_3)_5CO_3]^+$. The average values of the isotope effect for the three measured compounds at 0 °C, are

$[Co(NH_3)_4CO_3]NO_3$	$[Co(en)_2CO_3]Cl$	$[Co(NH_3)_5CO_3]NO_3$
0.8746 ± 0.0057	0.9873 ± 0.0066	1.000 ± 0.0055

The pentammino derivative does not exhibit an isotopic effect either.

To explain this distinct $^{14}CO_3{}^{2-}$ exchange behavior, Stranks considered that the $[Co(en)_2CO_3]^+$ ion quickly passes, by solvent action, to $[Co(en)_2HCO_3H_2O]^{2+}$, behaving in respect to $^{13}CO_3{}^{2-}$ exchange as the pentammino derivative. The same will happen to the tetrammino derivative but the difference is attributed to a rechelation equilibrium. This equilibrium for $[Co(en)_2CO_3]^+$ and $[Co(NH_3)_4CO_3]^+$ should be quite different.

The mechanism suggested by Stranks for this rechelation step involves the active heptacoordinated complex



A general normalization of the interchange mechanisms designed to cover all known cases was presented as follows:

Step 1 Protonation of CO_3^{2-} ligand.

$$[Co(NH_3)_4CO_3]^+ + H_3O^+ \rightleftarrows [Co(NH_3)_4HCO_3H_2O]^{2+}$$

$$[Co(en)_2CO_3]^+ + H_3O^+ \rightleftarrows [Co(en)_2HCO_3H_2O]^{2+}$$

$$[Co(NH_3)_5CO_3]^+ + H^+ \rightleftarrows [Co(NH_3)_5HCO_3]^{2+}$$

Step 2 exchange

Two processes are possible, one of which predominates at high CO_3^{2-} concentration:

a) ionic collision, *e.g.* for the tetrammine this will be

$$[Co(NH_3)_4HCO_3H_2O]^{2+} + + H^{14}CO_3^- \rightleftarrows [Co(NH_3)_4H^{14}CO_3H_2O]^{2+} + HCO_3^-$$

This reaction apparently replaces the "direct" exchange mechanism proposed earlier[106].

b) Total aquation, *e.g.* for the tetrammine, this would be

$$[Co(NH_3)_4HCO_3H_2O]^{2+} + H_2O \rightleftarrows [Co(NH_3)_4(H_2O)_2]^{3+} + HCO_3^-$$

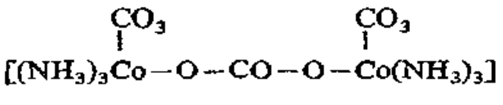
$$[Co(NH_3)_4(H_2O)_2]^{3+} + H^{14}CO_3^- \rightleftarrows [Co(NH_3)_4H^{14}CO_3H_2O]^{2+} + H_2O$$

$$[Co(NH_3)_4H^{14}CO_3H_2O]^{2+} \rightleftarrows [Co(NH_3)_4{}^{14}CO_3]^+ + H_3O^+$$

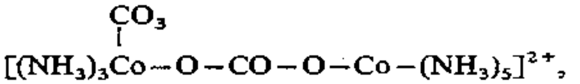
Holden and Harris[107] almost simultaneously reported an other interpretation of the behavior of carbonato tetrammino Co^{III} and carbonato bis-ethylenediamino Co^{III} ions in connection with this isotopic effect, and attributed the difference to the rapid aquation of $[Co(en)_2CO_3]^+$, due to the strain introduced by the (en) groups in the hexacoordinated structure. The racemization mechanism is said to be very complicated in regards to the interchange.

In 1955 Saito and Lazard[108] determined once again the interchange constants and arrived at the same values, but they attributed the result for $[Co(NH_3)_4CO_3]^+$ to the presence of unidentified impurities. They suggest the probable existence of some dinuclear and other impurities:

$$[(NH_3)_5Co-O-CO-O-Co-(NH_3)_5]^{3+},$$



$$[(NH_3)_3\overset{\overset{\textstyle CO_3}{|}}{Co}-O-CO-O-\overset{\overset{\textstyle CO_3}{|}}{Co}(NH_3)_3]$$



$$[(NH_3)_3\overset{\overset{\displaystyle CO_3}{|}}{Co}-O-CO-O-Co-(NH_3)_5]^{2+},$$

$$[(NH_3)_5Co-O-CO-NH_2]^{2+},\ [(NH_3)_4Co^{OCONH_2}_{OH}]^{+}.$$

This hypothesis would imply discarding the structural considerations used by Harris and Stranks and their coworkers.

There is no experimental evidence to prove the existence of any of the suggested "impurities" producing the "apparent" isotopic effect. Nevertheless, this is a sensible guess in the face of the unexpected isotopic effect, considering the rapid hydrolytic decomposition process of $[Co(NH_3)_4CO_3]^+$ ion. In Co^{II} ammines the formation of dinuclear adducts has been demonstrated[109] by direct oxidation in solution. Some further research has been suggested[110].

The exchange mechanism of $^{14}CO_3{}^{2-}$ ion was again considered by Stranks[44] bearing in mind that Taube's studies with O^{18}, show that the Co–O bond is not altered by aquation in the case of $[Co(NH_3)_5CO_3]^+$ and that only one such bond breaks in $[Co(NH_3)_4CO_3]^+$. This paper contains experimental information about the action of light, isotopic effect, surface, reactant concentration, temperature, ionic strength, all variables plotted as functions of $T_{\frac{1}{2}}$.

The mechanism interpretation follows a double path:

1) Ionic

Same as before: protonation–interchange–deprotonation

2) Aquation

Three alternate ways are possible:

A) Co–O rupture. This is the same mechanism used in the interpretation of previous reports and is not in accord with Hunt, Rutenberg and Taube[33,48].

For the pentammine:

$$\text{aquation } [Co(NH_3)_5HCO_3]^{2+} + H_2O \rightleftarrows [Co(NH_3)_5H_2O]^{3+} + HCO_3{}^-$$

$$\text{exchange } [Co(NH_3)_5H_2O]^{3+} + H^{14}CO_3{}^- \rightleftarrows [Co(NH_3)_5H^{14}CO_3]^{2+} + H_2O$$

followed by deprotonation and rechelation of the labelled complex.

B) C–O rupture and H migration.

$$[Co(NH_3)_5HCO_3]^{2+} \rightleftarrows [Co(NH_3)_5OH]^{2+} + CO_2$$

$$[Co(NH_3)_5OH]^{2+} + {}^{14}CO_2 \rightleftarrows [Co(NH_3)_5H^{14}CO_3]^{2+}$$

and also deprotonation and rechelation.

C) C–O rupture without H migration.

$$[Co(NH_3)_5HCO_3]^{2+} \rightleftarrows [Co(NH_3)_5O]^{+} + HCO_2{}^{+}$$

$$[Co(NH_3)_5O]^{+} + H^{14}CO_2{}^{+} \rightleftarrows [Co(NH_3)_5H^{14}CO_3]^{2+}$$

The $CO_3{}^{2-}$, $HCO_3{}^-$, CO_2 equilibria must be included for full consideration of the system. The rate law corresponding to all these three schemes will be the same, thus the problem cannot be kinetically resolved. Mechanism B is the most likely

TABLE 1

CARBONATO COMPLEXES OF COBALT(III)

	Pure ammine series	*Mixed ammines series*	*No ammin ligand*
CO_3H^-	$[Co(NH_3)_5CO_3H]X_2$* $X = Br^-, NO_3^-, S_2O_6^{2-}$ (1) (2)	(*trans*?) $[Co(NH_3)_4NO_2CO_3H]NO_3 \cdot H_2O$ (1)	
CO_3^{2-} monodentate (monosubstituted)	$[Co(NH_3)_5CO_3]X$ $X = Cl^-, Br^-, I^-, SeO_4^{2-}, NO_3^-,$ $C_2O_4^{2-}, CO_3^{2-}$ $[Cr_2(C_2O_4)_4(OH)_2]^{4-}$ (1) (2)	(*fac* or *mer*) $(NH_4[Co(NH_3)_3C_2O_4CO_3]$ (2) (3)	
CO_3^{2-} monodentate (disubstituted)	(*trans*?) $NH_4[Co(NH_3)_4(CO_3)_2]$ (2) (3)		
CO_3^{2-} bidentate (monosubstituted)	$[Co(NH_3)_4CO_3]X$ $X = F^-, Cl^-, Br^-, I^-, ClO_4^-, OH^-,$ $HSO_3^-, SO_4^{2-}, NH_2SO_3^-, S_2O_6^{2-},$ $SeO_4^{2-}, NO_3^-, CO_3^{2-}, HCO_3^-, C_2O_4^{2-},$ $SCN^-, MoO_4^{2-}, WO_4^{2-}, CH_3SO_3^-,$ $[Sb(OH)_6]^-, [Bi(S_2O_3)_2]^-, [PbCl_6]^{2-},$ $CrO_4^{2-}, Cr_2O_4^{2-}$, malonate, $[(C_2O_4)_4Co_2(OH)_2]^{4-}$. (1) (2)	(*trans* NH_3) $M[Co(NH_3)_2(NO_2)_2CO_3]$ $M = K^+, [Co(NH_3)_6]^{3+}, [Co(en)_3]^{3+},$ PyH^+. (10) (11) (12) *mer* $K_2[Co(NH_3)(NO_2)_3CO_3]$ (14) *cis*, *trans* $[Co(NH_3)_2(en)CO_3]Cl$ (1) (2) *cis*, *trans* $K[Co(NH_3)_2(C_2O_4)CO_3]$ (16)	$[Co(NN)_nCO_3]X$ X = various anions (NN) = (en) (1) (2) (17); pn, tn, ptn, dipy, phen, (1) (2) (18) ata, edda (16) gly, L-Ala, L-val (19) $K_3[Co(NO_2)_4CO_3]$ (15)
CO_3^{2-} bidentate (disubstituted)	*cis*, *trans* $K[Co(NH_3)_2(CO_3)_2]$ (21) (22) (23)		$K[Co(en)(CO_3)_2] \cdot H_2O$ (2) (10) (25) *trans* $K_3[Co(NO_2)_2(CO_3)_2] \cdot 2H_2O$ (24)
CO_3^{2-} bidentate (trisubstituted)			$M_3[Co(CO_3)_3]$ $M = Co^{3+}, K^+, Na^+, [Co(NH_3)_6]^{3+}$ (1) (66)
CO_3^{2-} bridge	$[Co_2(NH_3)_{10}CO_3](SO_4)_2$ (2) (26) $[Co_2(NH_3)_6(CO_3)_3] \cdot 3H_2O$ (1)		$K_8[Co_2(NO_2)_8(CO_3)_3] \cdot 2H_2O$ (24)

* Water will be omitted in general formulas.

References are given in parentheses.

Related compounds: monodentate carboxylato derivatives: monosubstituted (1) (2) (4) (5) (6); disubstituted (1) (2) (7) (8) (9); bidentate carboxylato derivatives: (1) (20).

especially for low CO_3^{2-} concentrations, where at low pH values CO_2 can be released.

With this B mechanism for the aquation path the authors present a table showing the calculated and experimental exchange constants. Some interesting comments are included on the influence of electronegativity and steric factors justifying the values obtained.

Further related studies were also reported. A comparison of the interchange behavior of intentionally different compounds yields interesting results. Complexes with the carbonato ligand and ligands other than ammine or ethylenediammine were studied in this way.

In 1958, Boyle and Harris[111] using the same kinetic method studied $[Co(tn)_2CO_3]^+$ and provided a mechanism which fit the experimental data. This mechanism includes an aquation and a ionic path. Recalculation of the previously studied cases is also included.

Values of the interchange rate constants for both simultaneous paths are given in Table 2.

TABLE 2

EXCHANGE RATE CONSTANTS FOR DIRECT AND AQUATION MECHANISMS

	Direct k_1 *l.mol*$^{-1}$ *min*$^{-1}$*25°*	*Aquation* k_2
$[Co(NH_3)_5CO_3]^+$	1×10^{8} (1)	9.3×10^{6}
$[Co(NH_3)_4CO_3]^+$	0.021	1.2×10^{6}
$[Co(en)_2CO_3]^+$	0.016	6.0×10^{5}
$[Co(tn)_2CO_3]^+$	0.0012	3.3×10^{-5}

(1) A constant is included in this figure.

The Table shows the high velocity of the ionic mechanism for the pentammine derivative and the very small aquation velocity path for $[Co(tn)_2CO_3]^+$.

The different velocities are explained by noting that in the pentammine the carbonato ligand shares the coordination sphere with 5 ammino groups whilst, in the bidentate complexe the aquation step introduces water into the coordination sphere. This water forms hydrogen bonds with the CO_3^{2-} group inbibiting protonation. The $[Co(NH_3)_5CO_3]^+$ species will protonate easily thus explaining the high direct mechanism contribution, while the other compounds do not. The pH is similarly explained.

Stranks[112] reexamined the direct part of the exchange mechanism and compared again the rate constants for the reactions at 25°.

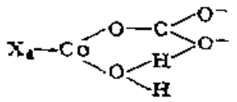
$$[Co(NH_3)_5CO_3]^+ + H^{14}CO_3^- \rightleftarrows [Co(NH_3)_5{}^{14}CO_3] + HCO_3^- \qquad k = 50\times 10^{-3}\ l.mol^{-1}sec^{-1}$$

$$[Co(NH_3)_4H_2O \cdot CO_3]^+ + H^{14}CO_3 \rightleftarrows [Co(NH_3)_4H_2O^{14}CO_3] + HCO_3^- \qquad k = 0.35\ l.mol^{-1}sec^{-1}$$

$$[Co(en)_2H_2OCO_3]^+ + H^{14}CO_3 \rightleftarrows [Co(en)_2H_2O^{14}CO_3]^+ + HCO_3^- \qquad k = 0.025 l.mol^{-1}sec^{-1}$$

$$[Co(tn)_2CO_3]^+ + H^{14}CO_3^- \rightleftarrows [Co(tn)_2H_2O^{14}CO_3]^+ + HCO_3 \qquad k = 0.01\ l.mol^{-1}sec^{-1}$$

The difference in velocity is again explained through the same H-bridge hypothesis. The formulation



is proposed and it is pointed out that a new 6-atom ring is produced, accounting for the stability against protonation. Steric factors are considered responsible for the low values obtained for the carbonato bis-trimethylenediamine Co^{III} ion.

Stranks points out in this article that due to the type of kinetic evidence there is some uncertainty in all the deductions; this should be kept in mind until independent proof is available.

In 1962, Pratt, Sherwin and Weston[113] studied the exchange reaction with *cis* $[Co(NH_3)_2(en)CO_3]^+$. It is found once again that the rate law is in accord with the presence of both direct and aquation mechanisms although the rate does not fit the order expected upon consideration of the other cases.

The observed values are:

$k_{direct} = 4.3\times 10^{-4}$ l.mol.$^{-1}$ sec^{-1}.

$k_{aq.} = 0.53\times 10^{-4}$ l.mol.$^{-1}$ sec^{-1}.

Later on, Lapidus and Harris[114] studied the bis-propylenediammino derivative $[Co(pn)_2CO_3]^+$. They used the same methods but they corrected the rate law and recalculated all known cases according to this new and slightly different rate law. The difference is based on the inclusion of an acid-base equilibrium in relation to the free CO_3^{2-} concentration.

The mechanism may be generalized as follows:

1. Aquo-dechelation equilibrium*
$[CoLCO_3]^+ + H_2O \rightleftarrows [CoLCO_3H_2O]^+$

2. Acid-base equilibrium
$[CoLCO_3H_2O]^+ + H_3O^+ \rightleftarrows [CoLHCO_3H_2O]^{2+} + H_2O$
$H_3O^+ + CO_3^{2-} \rightleftarrows HCO_3^- + H_2O$

---

* L means all other ligands.

3. Direct exchange

$$[CoLHCO_3H_2O]^{2+} + H^{14}CO_3^- \rightleftarrows [CoLH^{14}CO_3H_2O]^{2+} + HCO_3^-$$

4. Aquation exchange

$$[CoLH^{14}CO_3H_2O]^{2+} + H_2O \rightleftarrows [CoL(H_2O)_2]^{3+} + H^{14}CO_3^-$$

Only protonated complexes and free CO_3^{2-} species undergo exchange and steps 1, 2 and 3 do not determine the reaction rate. The simplified rate law has this form:

$$R = k'\alpha\beta ab + k''\alpha a$$

where a and b are the total carbonate ion and free carbonate ion concentrations respectively and α and β a combination of constants and $[H^+]$. The recalculated values for 25 °C are given in Table 3.

TABLE 3

RATE CONSTANT VALUES FOR DIFFERENT PATHS

	Direct $10^2 k'$ $M^{-1}min^{-1}$	*Aquation* $10^4 k''$	*Protonation* $10^{-9} k_2$	*E'act* *Kcal mol*$^{-1}$	*E''act.*
$[Co(NH_3)_5CO_3]^+$	32	470	6.26	16	20
$[Co(NH_3)_4CO_3]^+$	4.2	7.5	6	17	21
$[Co(en)_2CO_3]^+$	1.4	6.5	9	17	23
$[Co(pn)_2CO_3]^+$	2.2	1.9	16	17	29
$[Co(tn)_2CO_3]^+$	0.11	0.39	61	25	25

Several theoretical aspects are considered in the discussion. The CO_3^{2-} ring opening, reaction 1, is justified by the high strain of the bidentate group which had already been experimentally observed by Barclay and Hoskins[115] in resolving the crystal structure of $[Co(NH_3)_4CO_3]Br$.

The absence of an isotopic effect with the pentammino derivative is also commented upon. The formation of a hydrogen bridge is again considered, and an ion pair activated complex is proposed instead of the heptacoordinated one. The continuity of the bimolecular rate constant values for the ionic mechanism in the tetrammino series is noticed and the variation in the values for the aquation path is considered in regard to a solvation layer. On the other hand, the activation energies are related to the protonation processes and basicity of CO_3^{2-} in the different compounds. The CO_3^{2-} reactivity is also analyzed.

Francis and Jordan[116,117] disagreeing wbith the rate constant values found for some of the involved equilibria, suggested that the exchange mechanism could be satisfactorily interpreted without any contribution from the direct mechanism, that is, using a hydrolytic path only. This point is still subject to controversy.

Further kinetic studies of the acid hydrolysis of some of these complexes have recently been reported utilising new techniques and developments (new and faster methods, computers) and the experience gained on the successful relationship of kinetic studies and mechanistic predictions with structural approaches.

Tong, Kean and Hall[118] studied the reaction

$$[Co(en)_2CO_3]^+ + 2H_3O^+ \rightleftarrows [Co(en)_2(H_2O)_2]^{3+} + CO_2 + H_2O$$

using spectral information (isosbestic point) found earlier for this system.

Two mechanistic pathways are considered which satisfy the experimental results.

a non-protonated pathway with the solution species $[Co(en)_2CO_3]^+$ hydrated with some water molecules

and a protonated pathway with the solution species $[Co(en)_2HCO_3H_2O]^{2+}$

The two paths could be simultaneous; other possibilities are disregarded.

The aquation rate for the compound between 2×10^{-4} and 4×10^{-3}M $[H^+]$ is:

$$\frac{d\,[Co(en)_2CO_3{}^+]}{dt} = 0.92\text{M sec}^{-1}$$

In 1965, Harris and Sastri[119] reconsidered this work[118] and reported kinetic studies of the acid hydrolysis of $[Co(pn)_2CO_3]^+$ and $[Co(tn)_2CO_3]^+$ for pH 1 to 5. They found a pseudo 1st order reaction at constant $[H^+]$.

The mechanism suggested is again slightly different:

$$[CoL_2CO_3]^+ + H_2O \rightleftarrows [CoL_2H_2OCO_3]^+$$

$$[CoL_2H_2OCO_3]^+ + H^+ \rightleftarrows [CoL_2H_2OHCO_3]^{2+}$$

$$[CoL_2H_2OCO_3]^+ + H_2O \rightleftarrows [CoL_2OHH_2O]^{2+} + HCO_3{}^-$$

$$[CoL_2H_2OHCO_3]^{2+} + H_2O \rightleftarrows [CoL_2(H_2O)_2]^{3+} + HCO_3{}^-$$

$$[CoLH_2OHCO_3]^{2+} + H_3O^+ \rightleftarrows [CoL_2(H_2O)_2]^{3+} + H_2CO_3$$

This scheme differs from that of Tong, Kean, and Hall in that the species with the ring open form of CO_3 will retain coordinated water as the protonation of $CO_3{}^{2-}$ to $HCO_3{}^-$ is going on.

The rate law from such a mechanism was checked using a computer and the agreement of calculated and experimental values is excellent. Nevertheless, Jordan and Francis[116] pointed out inconsistencies in some of the constants used by Harris and Sastri and they suggest the following mechanism:

$$[Co(en)_2CO_3]^+ + OH^- \rightarrow [Co(en)_2OHCO_3]^+$$

$$[Co(en)_2OHCO_3]^+ + 2H^+ \rightarrow [Co(en)_2H_2OCO_3H]^{2+}$$

$$[Co(en)_2OHCO_3H]^+ + H_2O \rightarrow [Co(en)_2OH(H_2O)_2]^{2+} + HCO_3{}^-$$

$$[Co(en)_2OHCO_3H]^+ + H^+ \rightarrow [Co(en)_2H_2OCO_3H]^{2+}$$

$$[Co(en)_2H_2OCO_3H]^{2+} + H_2O \rightarrow [Co(en)_2(H_2O)_2]^{3+} + HCO_3{}^-$$

$$[Co(en)_2CO_3H]^{2+} + H_3O^+ \rightarrow Co(en)_2(H_2O)_2{}^{3+} + H_2CO_3$$

This is purely an aquation mechanism and accounts for the experimental rate law, excluding any contribution from the direct mechanism.

Finally Das Gupta and Harris[120] reported a spectrophotometrically followed kinetic study of the aquation of $[Co(tren)CO_3]^+$ (tren = 2,2′,2″ triaminotriethylamine), pH range 0.3–4.5.

A multiple-step mechanism is proposed: dechelation with protonation and aquation, dechelation and aquation, deprotonation of aquo-bicarbonato and decarboxylation producing hydroxo-aquo ions.

Research designed to test the existence of a similar type of mechanism in similar compounds was undertaken by Fialkov and Penasyuk[121,122] on the sulfato derivatives $[Co(NH_3)_4SO_4]^+$, $[Co(NH_3)_5SO_4]$. They found two concurrent mechanisms.

Banaclough and Murray[123] studied the hydrolysis of $[Co(en)_2SO_4]ClO_4$ and the kinetics were very different from those of the carbonato ammino Co^{III} compounds.

Summing up the total work on this field we may conclude that kinetic and $^{14}CO_3^{2-}$ tracer exchange reaction studies establish that the CO_3^{2-} ligand undergoes aquation–protonation being transformed to an aquo-bicarbonato species. The direct exchange contribution in the rate law has been accepted in some cases but recently it has been questioned.

Further work in this area is expected. The existence of a very rapid initial step is now being considered by using "flow" techniques. The existence of so many schemes for the reaction differing often but little, is typical of kinetic-mechanistic research.

^{18}O studies on aquation.—Hunt, Rutenberg and Taube[33] using ^{18}O tracer techniques studied the aquation reaction

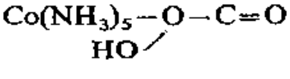
$$[Co(NH_3)_5CO_3]^+ + H_2O + 2H^+ \rightarrow [Co(NH_3)_5H_2O]^{3+} + H_2CO_3$$

and found that it proceeds without rupture of the Co–O bonds.

The experiments consisted in dissolving $[Co(NH_3)_5CO_3]NO_3$ in ^{18}O enriched water, cooling to 0° and adding HCl. After the aquation reaction is complete, the $[Co(NH_3)_5H_2O]^{3+}$ produced is precipitated by $HgCl_2$; the complex is then dehydrated and the water examined by mass spectrography. ^{18}O does not appear in the water eliminated from the complex; this means that oxygen previously bonded to the cobalt atom from the CO_3^{2-} group remained intact through the aquation reaction. The aquation process then is a substitution reaction retaining the original Co–O bond.

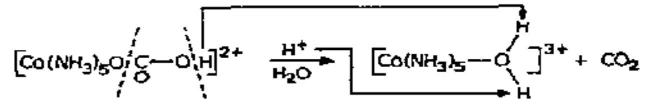
The Lamb and Mysels kinetic experiments[31] have shown that the rate of aquation is proportional to the $[Co(NH_3)_5CO_3]^+$ concentration.

This ion can be considered a derivative of H_2CO_3 as:

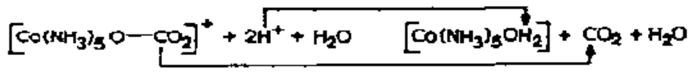


$$Co(NH_3)_5{-}O{-}\underset{HO\diagup}{C}{=}O$$

The decomposition of $H_2CO_3 \rightleftarrows H_2O + CO_2$ should be the same for the complex which should lose its CO_2 as



for the protonated species and

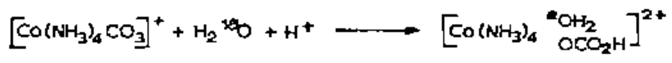


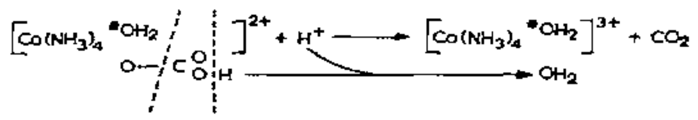
if no protonated species is considered.

Posey and Taube[48] employed a similar procedure to study the aquation of $[Co(NH_3)_4CO_3]^+$. The results showed that the $[Co(NH_3)_4(H_2O)_2]^{3+}$ produced by total aquation in:

$$[Co(NH_3)CO_3]^+ + 2H^+ + H_2O \rightarrow [Co(NH_3)_4(H_2O)_2]^{3+} + CO_2$$

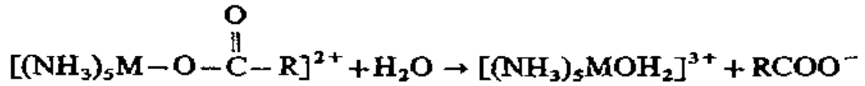
retains ½ of the original $CO_3{}^{2-}$ oxygen bond, the second being from water. The possibility of an exchange between both oxygen atoms has been rejected by checking the isotopic composition of CO_2 produced. This result means that the aquation process opens one oxygen bond without affecting the other. The open bond becomes the site for the entrance of the solvent oxygen.



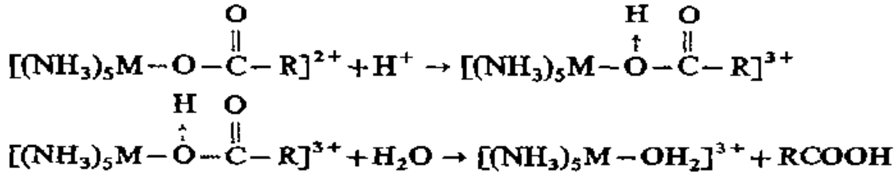


The first step should be rapid and the second slow, (rate determining). The activated complex of the second step should have a hydrogen bridge between water and the CO_3H^+ oxygen. The maintenance of the Co–O bond in $[Co(NH_3)_5CO_3]^+$ case was confirmed by Bunton and Llewellyn[45] who pointed out that this hydrolysis should be looked upon as a decarboxylation process rather than a hydrolytic one. (See page 173).

After these two fundamental reports some other carboxylato derivatives were studied but the results do not support a generalization about the way the carbonato group leaves the complex matrix[45]. Monacelli, Basolo and Pearson[131] suggested that the carboxylato pentammino Co^{III} complexes should follow two simultaneous paths:

1) 

$$[(NH_3)_5M-O-\overset{\overset{\displaystyle O}{\|}}{C}-R]^{2+}+H_2O \rightarrow [(NH_3)_5MOH_2]^{3+}+RCOO^-$$

2) 

$$[(NH_3)_5M-O-\overset{\overset{\displaystyle O}{\|}}{C}-R]^{2+}+H^+ \rightarrow [(NH_3)_5M-\overset{\overset{\displaystyle H}{\uparrow}}{O}-\overset{\overset{\displaystyle O}{\|}}{C}-R]^{3+}$$

$$[(NH_3)_5M-\overset{\overset{\displaystyle H}{\uparrow}}{O}-\overset{\overset{\displaystyle O}{\|}}{C}-R]^{3+}+H_2O \rightarrow [(NH_3)_5M-OH_2]^{3+}+RCOOH$$

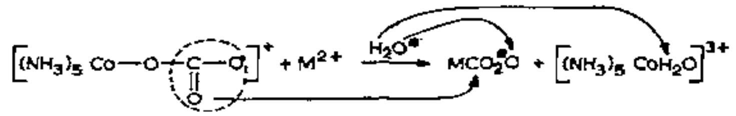
one of them involving protonation of the carboxylic ligand. The evidence for such a protonation was also considered.

The authors experimental work shows 1st order in $[H^+]$. The views of Bunton and Llewellyn[45] are also discussed in this report.

Another interesting reaction was considered by Jordan, Sargeson and Taube[46]. They found that precipitation of a metal carbonate (MCO_3) by reaction of $[Co(NH_3)_5CO_3]$ with cations such as Hg^{2+}, Pb^{2+} and Ba^{2+}, involves an aquation process

$$[Co(NH_3)_5CO_3]^+ + M^{2+} + H_2O \rightarrow [Co(NH_3)_5H_2O]^{3+} + MCO_3$$

and is at least 100 times slower for Ba^{2+} than for Pb^{2+} and Hg^{2+}, which precipitate rapidly. By using ^{18}O as tracer they concluded that in the cases of rapid precipitation no ^{18}O is found in the complex; this implies an undisturbed Co–O bond and CO_2 as the leaving group, instead of $CO_3{}^{2-}$ which would be the simplest guess.



The Ba^{2+} reaction should proceed by a combination of both the C–O and Co–O bond rupture processes.

Polarographic research on the aquation of $[Co(NH_3)_4CO_3]^+$ was undertaken by Ralea, Burlacu and Giurgiu[34]. They were able to follow the aquation process by the reduction of the first polarographic wave as a function of time. Parallel experiments were set up at various pH values.

The first polarographic wave of this complex divides into two in acid solution, implying the coexistence of two species.

Using the Mathieu scheme for interpretation:

$$\begin{array}{lll} [CoA_4X_2]^+ + H_2O \rightleftarrows [CoA_4XH_2O]^{2+} + X^- & & \\ [CoA_4XH_2O]^{2+} + H_2O \rightleftarrows [CoA_4(H_2O)_2]^{3+} + X^- & & \\ \quad -H^+ \upharpoonleft\downharpoonright +H^+ \qquad\qquad -H^+ \upharpoonleft\downharpoonright +H^+ & \text{(slow)} & \\ [CoA_4OHX]^+ + H_2O \rightleftarrows [CoA_4H_2OOH]^{2+} & \text{(fast)} & \end{array}$$

The last equation involving formation of hydroxo-aquo or acido-hydroxo species can be neglected if acid is added.

Using acido-pentammino, diaquotetrammino and acido-aquo tetrammino polarographic waves for comparison with the experimental curves from different states of the $[Co(NH_3)_4CO_3]^+$ aquation system, the authors conclude that the final aquation species is an acido-aquotetrammino Co^{III}. The aquation process corresponds to

$$[Co(NH_3)_4CO_3]^+ + H_2O \rightarrow [Co(NH_3)_4CO_3H_2O]^+$$

and at convenient pH values (3.29) should produce $[Co(NH_3)_4HCO_3H_2O]^{2+}$.

Using a conductiometric method they found that the main product of the aquation is the first cited, $[Co(NH_3)_4CO_3H_2O]^+$.

The measured rates of aquation are:

	$k_{15°}$	$k_{20°}$	$k_{25°}$	$k_{30°}$	(sec^{-1})
pH = 3.29	1.194×10^{-4}	2.038×10^{-4}	3.07×10^{-4}	------	
pH = 4.10	-------	1.024×10^{-4}	1.666×10^{-4}	2.523×10^{-4}	

The reaction behaves as first order in $[H^+]$ and is considered of the SN1 type.

In 1964, the same authors[124] used similar reasoning in explaining polarograms from other complexes. The oscillo-polarographic work also supports in a general way the aquo-acido tetrammino step for the aquation of tetrammino derivatives.

(ii) *Mechanisms of base-hydrolysis*

The reaction:

$$[Co(NH_3)_5X]^{2+} + OH^- \rightarrow [Co(NH_3)_5OH]^{2+} + X^-$$

is a kind of substitution reaction, whose mechanistic problems can be conveniently presented first, in a synthetic and general way.

The main problems with these reactions are as follows: a) the reactions are kinetically of second order, the rate of complex consumption being proportional both to the complex and OH^- concentrations; b) the SN2 and SN1CB mechanisms have been proposed but a decision about the general adoption of any of them has not been possible[125,126]. According to the new Langford and Gray[127] symbolism, it will correspond to type Ia, (interchange associative activation); c) the stereochemical aspects of the entrance of a group during substitution present a particular problem for the OH^- group due to the special characteristics of hydroxo in regard to protonation.

Several kinetic investigations on the base-hydrolysis of carbonato and carboxylato ammines of Co^{III} have been carried out. The principal studies utilise pentammino derivatives but some consideration has also been given to tetrammino compounds.

Basolo, Bergman and Pearson[128] measured the rate of base-hydrolysis of several carboxylato-pentammino Co^{III} derivatives, using a series of substituted acetic acids. The velocities obtained were found to depend on the relative ligand basicity but not on size.

This independence in relation to size led the authors to believe that the OH^- attack on the complex localized on the opposite site of the leaving group[129]. A similar study concerning $[Co(en)_2(RCO_2)_2]$ was published[130] by Illuminati and coworkers.

Using an ^{18}O tracer Bunton and Llewellyn[45] worked on a series of carboxylate pentammino Co^{III} perchlorates. The carboxylato ligands included acetato, monochloroacetato, trichloroacetato, and trifluoroacetato.

The tracer is followed on the carboxylic group instead of the complex due to the further exchange that the complex undergoes with solvent. Two experimental procedures were used. One of them extracts the leaving carboxylic acid using ether and converts it to the silver or sodium salt. Carbon dioxide is liberated therefrom and its isotopic composition determined using a mass spectrometer. The other technique separates the complex by using alumina. The neutral solution is vacuum evaporated and bromine decomposed, etc. The results indicate that aquation for acetato and trifluoroacetato pentammino Co^{III} goes on with Co–O rupture. Base-hydrolysis of all the complexes studied also entails a Co–O rupture mechanism with the exception of the trifluoroacetato derivative which maintains this bond, breaking the C–O bond.

The SN2 and BAC2 mechanisms, the last corresponding to ester hydrolysis and adapted to the special trifluoroacetato pentammino Co^{III} base-hydrolysis, are discussed.

Cagliotti and Illuminati[132] using ^{18}O carried out a study of base hydrolysis of some diacido complexes of the types $[Co(en)_2(OAc)(OH)]^+$ and $[Co(dipy)_2(OAc)_2]^+$. The dipyridine derivatives show an $[OH^-]$ independant base hydrolysis rate. They argued that these complexes cannot form a conjugate base intermediate as observed elsewhere (SN1CB).

Jones and Thomas[5] using a group of new compounds, carboxylato pentammino Co^{III} derivatives, measured their base-hydrolysis rates showing their polarity dependence on the carboxylato group. The observed kinetics can be interpreted by using an SN2 or SN1CB mechanism. Also, the BAC2 mechanism suggested for the trifluoroacetate derivative should be possible. The reaction is 2nd order and the leaving carboxylato ligand breaks the Co–O bond.

Angerman and Jordan[133] reported the kinetics of base-hydrolysis for oxalato, fumarato and maleato, pentammino Co^{III} compounds. They show similar behavior resulting in a 1st order reaction in both reactants, $[OH^-]$ and [Complex].

The oxalato pentammino Co^{III} base hydrolysis does not behave similarly. It shows a 1st order term in $[OH^-]$ and a 2nd order term in $[OH^-]$. The authors consider the C–O rupture mechanism for this case.

Francis and Jordan[117] studied the kinetics of base hydrolysis of $[Co(NH_3)_5CO_3]^+$. The rate law observed is:

$$-\frac{d(T)}{dt} = k_1[Co(NH_3)_5CO_3H^{2+}] + k_2[Co(NH_3)_5CO_3{}^+]\,[OH^-]$$

which can be simplified in terms of $[OH^-]$ as:

$$-\frac{d\ln[\text{complex}]}{dt} = k_1[OH^-]^{-1} + k_2[OH^-]$$

The measurements cover alkali concentration from 0.02 to 1.00M NaOH.

The $k_2[OH^-]$ term is attributed to a normal base hydrolysis of $[Co(NH_3)_5CO_3]^+$ ion and the $k_1[OH^-]^{-1}$ to aquation of $[Co(NH_3)_5HCO_3]^{2+}$. They also mention the possibility of a third term. From the data thus obtained, they were able to calculate the formation constant for the bicarbonato pentammino complex:

$$K_f = \frac{[Co(NH_3)_5HCO_3{}^{2+}]\,[OH^-]}{[Co(NH_3)_5OH^{2+}]\,[HCO_3{}^-]} = 2.97 \times 10^{-4}$$

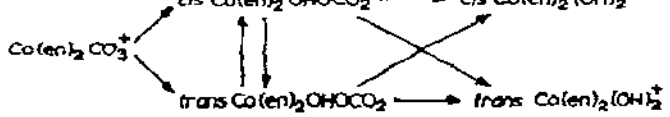
By comparing results and using further correlations, the authors suggested a SN1CB type of mechanism.

Finally, there is a report from Carunchio, Illuminati, and Ortaggi[198] on the kinetics of base hydrolysis of the cis-trans isomers of di-acetato, bis-ethylenediammino Co^{III} ions. This phenomenon takes place in two steps the first being faster. The reaction is first order in both reactants [complex] and $[OH^-]$. The mechanism is said to be dissociative.

With reference to the base hydrolysis of bidentate carbonato compounds the work of Scheidegger and Schwarzenbach[134] consisting of rapid pH titrations might be mentioned. At alkaline pH values the CO_3Me ring opens (see section D).

The production of dihydroxo derivatives at high pH values has been polarographically demonstrated as already cited[124].

During the course of his thesis work, J. Hargis[135] studied the kinetics of base hydrolysis of $[Co(en)_2CO_3]^+$ using the 323 mμ spectral maximum. The reaction is pseudo first order in [complex] and the suggested mechanism is similar to that reported earlier[134].



The isomerization reactions are $[OH^-]$ independent and the other reactions are 1st order in $[OH^-]$. All of them are 1st order in [complex]. Values for various combined constants are given.

In conclusion all the studies confirm that base-hydrolysis of carbonato ammino Co^{III} derivatives is an OH^-–CO_3^{2-} substitution reaction, showing 1st order kinetics in both reactants. A uniformily accepted mechanism is not available but most opinions favour a SN1CB type.

D. RING OPENING PROCESS

Another interesting aspect of the chemistry of the carbonato ligand is the question of the ring opening mechanism. Recently several studies have been directed to this question.

McKenzie, O'Conner and Odell[39] carried out ^{18}O tracer techniques to approach this problem in $[CoA_4CO_3]^+$ compounds; they used $[Co(NH_3)_4CO_3]Cl$ and found evidence of the existence of a fast dechelation equilibrium.

Experiments were carried out in closed vessels containing enriched ^{18}O water kept at constant temperature. An aliquot was transferred to a Y tube to allow for perchloric acid decomposition of the complex at the desired time. The CO_2 evolved was condensed and its isotopic composition analyzed by mass spectography. The exchange fraction was calculated from the data. The exchange rate velocity was:

$$k(H_2O)^n = 3 \times 0.693/T_{\frac{1}{2}}$$

The factor 3 takes care of the fact that all three oxygen atoms are exchangeable. The reaction is 1st order in [complex]. The exchange constant does not depend on pH.

The small curvature of the experimental data plot is attributed to aquation by fast CO_3^{2-} interchange with free CO_3^{2-}. If free CO_3^{2-} is eliminated using $BaCl_2$, the curvature disappears.

The authors believe the precipitation is a way of forcing the chelate ring to close up. Since it has been conclusively proven[115] that CO_3^{2-} is in a bidentate form in the crystalline state, and that it undergoes a rapid dechelation in water, it is interesting to understand how the chelation may come about. By adding an excess of $NaClO_4$ together with $BaCl_2$, the formation of free CO_3^{2-} is eliminated.

The tracer experiments led to one of three possible ways for the linkage of CO_3^{2-} in solution:

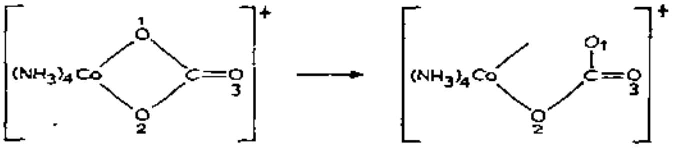
a) chelate; one oxygen atom free for exchange.

b) permanently dissociated: the three oxygen atoms free for exchange[32].

c) reversibly dissociated at one end; the three oxygen atoms will be equivalent to exchange.

Total separation of the CO_3^{2-} group from the cobalt atom is disregarded on the basis of other general experimental evidence (*e.g.* exchange kinetics).

The authors conclude that the real process is *c*; this means that the bidentate carbonate dissociates by one oxygen atom each time and since the ^{18}O exchange is fast the three oxygen atoms behave identically from the kinetic point of view. Schematically



1 and 3 remain free for exchange.

In a successive event opening 2 and 3 should be liberated for exchange and so on. The possibility *a* was discarded because in several experiments exchange rose above 50%.

Some experiments were carried out under conditions where ring formation was forced before decomposition and the isotopic composition of the CO_2 was examined. In these experiments the conclusion is again that all three oxygen atoms are equivalent as far as exchange is concerned, whether the dissociation fits scheme *b* or *c* in solution.

The *c* mechanism is in accord with Posey and Taube[48] who stated that the two oxygen bonds in the chelated carbonato do not differ from each other during aquation.

The observation of ring closing is also in accord with our observations on the transformation of $[Co(NH_3)_5CO_3]X$ into $[Co(NH_3)_4CO_3]X$, under certain preparative conditions.

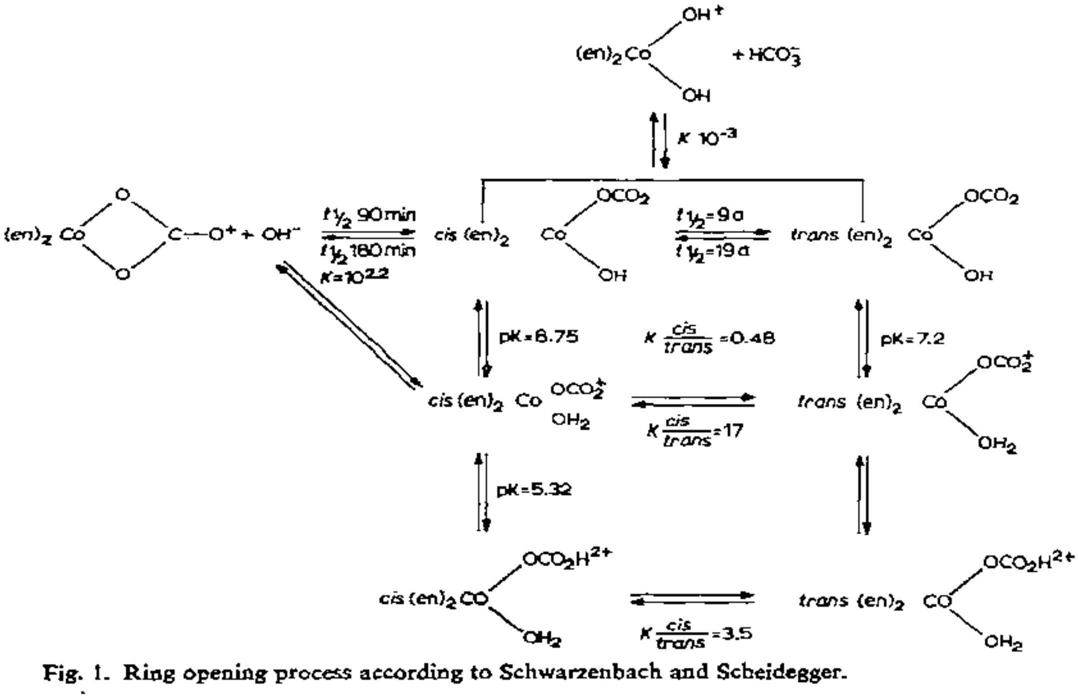
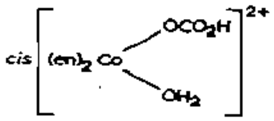


Fig. 1. Ring opening process according to Schwarzenbach and Scheidegger.

Using new methods now developed for the experimental study of fast reactions (rapid flow apparatus), Scheidegger and Schwarzenbach[134] were able to measure pH values very quickly, (time of the order of 5×10^{-3} sec) for the reaction $Co(en)_2CO_3^+ + OH^-$. The main conclusion reached was that tbe chelate ring does exist in solution.

The ring opening process produces several species of a different degree of protonation depending on pH. A schematic interpretation is considered in Fig. 1, which includes some equilibrium constant data.

The chelate structure remains aprotic in the pH range 3–11, but when it opens the donor–acceptor character of the new structure establishes the existence of a dibasic acid in the system



The dissociation constants for this acid are given by the authors (see Fig. 1). Further discussions of this system are available[116,120].

E. PHYSICAL PROPERTIES

i) *Visible and ultraviolet spectroscopy*

The crystalline $[Co(NH_3)_5CO_3]X$ and $[Co(NH_3)_4CO_3]X$ compounds are red and the $M_3[Co(CO_3)_3]$ compounds deep green.

The chromophore is quasioctahedrally N and O coordinated cobalt(III). The variation in the spectra from one complex to another is determined by the influence of the substituent groups. The solution spectra of $[Co(NH_3)_5CO_3]^+$ and $[Co(NH_3)_4CO_3]^+$ have been reported many times[22,73–79]. The species may be stabilised in various ways *e.g.* $4N(NH_4)_2SO_4$[75] low temperature (3–4°)[79]; Na_2CO_3 at various conc[44], methanol–water can also be used[80] as solvent.

The spectrum exhibits two principal maxima as follows:

$\underline{[Co(NH_3)_4CO_3]NO_3\tfrac{1}{2}H_2O.}$

1st band. ν_1 max. = 524 mμ. $w_{\frac{1}{2}}$ = 125 mμ. log ε = 2.02.

2nd band. ν_2 max. = 359 mμ. $w_{\frac{1}{2}}$ = 50 mμ. log ε = 4.09.

There is an inflexion at 300 mμ and a charge transfer band at 238 mμ.

$\underline{[Co(NH_3)_5CO_3]NO_3 \cdot H_2O}$

1st band. ν_1 max. = 510 mμ. $w_{\frac{1}{2}}$ = 110 mμ. log ε = 1.93.

The 2nd band is not defined. It appears as an inflexion at 370 mμ on the edge of the charge transfer absorption[79]. In checking the purity of the compounds the extinction coefficient of the ν_1 maxima, $\log \varepsilon (NO_3) = 2.02$, $\log \varepsilon(Br\ \text{or}\ Cl) = 2.00$, for the tetrammine derivatives and 1.93 for the pentammine (10^{-2}M in $4N(NH_4)_2SO_4$) can be conveniently used.

Some correlations from the spectra observed with these and other compounds have been emphasized.

The bidentate CO_3^{2-} ligand produces a hypsochromic effect on the 1st maxima and according to the rules[73,81] derived from wider studies this gives us a clue to the relative stability of this species. The pentammino should be the more stable.

The band shifts resulting from substitution of different groups into pentammines and tetrammines were considered by Yamada and Tsuchida[77] who established a "hyperchromic series" as follows: NCS^-, CrO_4^{2-}, SO_3^{2-}, NO_2^-, CO_3^{2-}, CrO_4^{2-}, en, OH^-, NO_3^-, SO_4^{2-}, Br^-, NH_3, Cl^-, H_2O.

If a ligand is substituted by another, the absorption bands shift to the red (bathochromic effect) or to violet (hypsochromic effect) according to the relative position of entering and leaving groups in the series. CO_3^{2-} is more hyperchromic than NH_3 so $[Co(NH_3)_5CO_3]^+$ will present a hypsochromic shift, vis a vis the hexammine.

This series is not the same as the spectrochemical series and the authors do consider the differences.

After 1950, our understanding of optical and other properties of complexes was clarified thanks to the development of Ligand Field Theory. We will not go through any discussion of this theory, but will simply state that the spectra of spin paired cobalt^{III} octahedral complexes show two bands, usually near 500 mμ and 330 mμ with a charge transfer band at somewhat higher energy. These two bands are assigned to the spin allowed *d-d* transitions:

$^1T_{1g} \leftarrow {}^1A_{1g}$ for the first (ν_1)

and

$^1T_{2g} \leftarrow {}^1A_{1g}$ for the second band (ν_2).

The energy difference between such states for Co^{III} in a perfectly octahedral field, will depend on the ligands and varies from 16,000 to 21,000 cm^{-1} (*ca.* 630–480 mμ) for 1st band and 24,000 to 29,000 cm^{-1} (420–350 mμ) for the second.

The values of the Dq and Racah B and C parameters are characteristic of a ligand. The introduction of substituting ligands affects the cubic symmetry. A substituted complex is no longer purely octahedral and the ligand field should induce some splitting in the orbital triplet energy levels. Nevertheless, if the symmetry is approximately octahedral the general features of the spectrum do not change much. This is the case with the spectra of $[Co(NH_3)_5CO_3]^+$ and $[Co(NH_3)_4CO_3]^+$.

An approximation for the calculation of band-maxima is based on the rule of average environment[82]. The $10Dq$ value for $[Co(NH_3)_4CO_3]^+$ can be taken as an average of the corresponding values of the parent octahedral species.

$10Dq$ for $Co(NH_3)_6{}^{3+} = 22.9\ Kk^{83}$

$10Dq$ for $Co(CO_3)_3{}^{3-} = 17.3\ Kk$

$$\text{For the tetrammine } 10\ Dq = \frac{4\times 22.9+2\times 17.3}{6} = 21.0\ Kk$$

If the $10Dq$ parameter is obtained from the experimental spectrum ($\nu_1 = 19{,}084$, $\nu_2 = 27{,}933$) using the Tanabe and Sugano diagram we find, $10Dq = 21{,}000$, $B = 636\ cm^{-1}$.

The rule of average environment appears confirmed. Similar calculations can be performed for $[Co(NH_3)_5CO_3]NO_3$ using $\nu_1 = 510\ m\mu$ and $\nu_2 = 335\ m\mu$ estimated from the reflectance spectrum. This gives $10Dq = 21.9\ Kk$ in fairly good agreement with 21–96 Kk obtained from tbe rule.

Both compounds are correctly considered to have Oh symmetry. Two bands are observed in the reflectance spectra of $[Co(NH_3)_4CO_3]NO_3 \cdot 0.5H_2O$ and $[Co(NH_3)_5CO_3]NO_3 \cdot 1.0H_2O$ at 525 and 370 mμ and 510 and 335 mμ respectively.

Single crystal absorption studies have been reported[84]. The observed band width of carbonato tetrammino Co^{III} complexes has been discussed by S. Crawford[85]. There are several factors determining the band width of complexes, *viz.* number of transitions, splitting energies, lifetime of excited states, etc.

A series of carboxylic acid chelated bis-ethylene-diamine complexes of Co^{III} were considered. The band width of $[Co(en)_2CO_3]^+$ is smaller than the others; this is explained on the basis of a better retention of the excited state because of the rigidity of the 4 membered ring, which the author suggests, should have 90° bond angles.

The most important factor determining the band width is the splitting of the electronic state and rigidity is a minor factor. The spectra of many other complexes have been reported[1,14,64,86–91].

(ii) *Infrared spectroscopy*

IR spectroscopy has been an excellent source of knowledge regarding the bonding in carbonate complexes. From a general point of view two principal steps can be distinguished in IR work on this subject: 1) description and empirical assignment of spectra features (1952–1962); 2) calculation of spectral details by applying newly developed methods (normal coordinate analysis) to structural models for the bonded $CO_3{}^{2-}$ and examination of the results vis a vis the experimental data.

Early work was carried out by Yoneda, Kida, and Kobayashi[136] who studied the aqueous solution spectra in the near IR of various compounds including $[Co(NH_3)_5CO_3]Cl$ and $[Co(NH_3)_4CO_3]NO_3$.

Merrit and Wiberley[137] reported the IR spectra of 19 complexes including $[Co(en)_2CO_3]ClH_2O$ and $[Co(NH_3)_4]NO_3 \cdot 0.5H_2O$, from 6–12 μ.

An absorption frequency at about 6 μ was assigned to a vibration of the NH_3 group. Nakamoto and co-workers[138] considered the effect of coordination on the IR spectra of complexes having mono and bidentate ligands. They found that coordination of a ligand will produce the following effects: 1) new bands, 2) separation of degenerate modes; 3) shifts in frequency and 4) variations in the intensity of some absorption frequencies.

The new absorption bands and the loss of degeneracy arise through changes in symmetry. The intensity changes are explained in terms of a modification of the type of vibration.

The IR spectra from 5000–400 cm^{-1} of SO_4^{2-}, CO_3^{2-} and $C_2O_4^{2-}$ compounds of both monodentate and bidentate character are reported[138] and Table 4 shows the spectral data assigned to the carbonato group.

TABLE 4

INFRARED FREQUENCIES OF THE CARBONATE GROUP

	symmetry	*frequencies*			
		ν_1	ν_2	ν_3	ν_4 cm^{-1}
CO_3^{2-} free	D_{3h}		879 F*	1415 MF	680 F
calcite	D_3		874 F	1430 MF	710 M
aragonite	C_s	1080	855 F	1470 MF	710 M 696 D
$[Co(NH_3)_6]Cl \cdot CO_3$	D_3		865 F	1390–1370 MF	680 M
$[Co(NH_3)_5CO_3]Br$	C_{2v}	1070 MD	848 F	1470 F–1370 F	750 D
$[Co(NH_3)_4CO_3]Cl$	C_{2v}	1025 M	837 F	1592 F–1255 F	752 M
$[Co(en)_2CO_3]Br$	C_{2v}	1015 M	825 F	1575 F–1278 F	757 M

* M = medium; F = strong; D = weak.

ν_1 is very weak and ν_3 a degenerate vibration in the free ion is split in the monodentate derivative, as a consequence of a lowering of the symmetry from D_3 to C_{2v}. In the bidentate CO_3^{2-} complexes, ν_1 is stronger and the splitting of ν_3 becomes greater.

It is noteworthy that in the complexes the symmetry of the CO_3^{2-} group is considered unchanged and the spectral differences arise through differences in the bond strength only.

H. Siebert[139] studied the IR spectra of 27 substituted ammines with oxoanions ligands and by a comparison thereof he assigned the anion ligand bands.

The symmetry of the oxoanion ligands decreases through coordination according to:

	free	*coordinated*
CO_3^{2-}	D_{3h}	C_{2v}
HCO_2^-	C_{2v}	C_s
$C_2O_4^{2-}$	V_h	C_{2v}

Gatehouse, Livingstone and Nyholm[140] reinterpreted the IR spectra of free and coordinated CO_3^{2-}. The Raman spectrum and the origin of molecular vibration were studied[3].

Table 5 shows frequencies for the free $CO_3{}^{2-}$. Tracers have been used for this detailed empirical assignment; *e.g.* for $BaCO_3$, 3 bands appear in IR, at 1420, 857 and 692 cm^{-1}. By using $Ba^{13}CO_3$ a shift of the 857 band to 832 cm^{-1} occurs, and this permits the assignment of these bands to the out-of-plane deformation of $CO_3{}^{2-}$.

TABLE 5

ASSIGNMENT OF THE VIBRATIONS OF THE FREE CARBONATE ION

Type	*Raman*	*IR*	*designation*	*cm^{-1}*	*origin*
A_1'	active	inactive	ν_1	1063	C–O sym. stretch
A_2'	inactive	active	ν_2	879	CO_3 out of plane def.
E'	active	active	ν_3	1415	C–O asym. stretch
E	active	active	ν_4	680	CO_3 in plane def. (or rocking)

The lowering of symmetry by coordination reveals itself in appearance of a new band (previously noticed by Duval, 1943) at 1050 cm^{-1} and in the separation of the ν_3 degenerate mode into two, ν_1 and ν_4, thus agreeing with Nakamoto *et al.*[138].

The assignment of frequencies upon coordination is shown in Table 6. A diagram is included[140] showing the features of the IR spectra for the various kinds of $CO_3{}^{2-}$ group (such as basic, complex, acid and those in organic compounds). These differences are enough to permit the use of this method for identification.

TABLE 6

ASSIGNMENT* OF THE VIBRATIONS OF A COORDINATE CARBONATE GROUP

Type	*designation*	*origin*
A_1	ν_3	CO_2 bend
A_1	ν_1	CO_2 sym. stretch
A_1	ν_2	CO stretch
B_2	ν_6	Non planar rock
B_1	ν_4	asym. stretch
B_1	ν_5	planar rock

*All frequencies are allowed both in the Raman and infrared.

Some further reports showing the same type of empirical assignments, justifying shifts and other changes, have been published. Lascombe[141] examined the variation in the infrared for mono and bidentate $CO_3{}^{2-}$.

Quagliano *et al.*[142] reconsidered the assignment for monodentate and bidentate complexes using deuteration as a guide. Frequencies observed at about 1600, 1300 and 850 cm^{-1} are assigned to deformations of the NH_3 group. Some frequencies are calculated theoretically to verify the correctness of the assignments.

Some interesting details emerge *e.g.* the 1604 cm^{-1} band in [Co(NH$_3$)$_4$CO$_3$]-Cl decreases a little on deuteration; this is interpreted by considering the band to be a superimposition of two bands, one from an N-H vibration and the second from a CO$_3$$^{2-}$ vibration. The 1268 cm^{-1} and 832 cm^{-1} bands do not change upon deuteration. Both are CO$_3$$^{2-}$ bands. The 1448 and 1364 cm^{-1} bands from [Co(NH$_3$)$_5$CO$_3$]I are assigned to stretching modes and a band at 908 cm^{-1} to a deformation mode of the monodentate carbonate group. The 1612, 1310 and 849 bands are attributed to NH$_3$. The interpretation of the IR spectral changes provides support for the existence of mono and bidentate CO$_3$ ligands in the above compounds. Other work on these systems has been published[15,143].

In 1962, Fujita, Martell and Nakamoto[144] using theoretical and methodological advances in IR spectroscopy, calculated the IR spectra of monodentate and bidentate CO$_3$$^{2-}$ groups bonded to Co^{III}.

The principal advance we refer to is called normal coordinate analysis.

In order to carry out a normal coordinate analysis of any group of atoms it is necessary to know all the structural details. At that time the absolute structure of the CO$_3$ ligand in complexes was unknown. The authors assumed therefore the structure shown in Fig. 2.

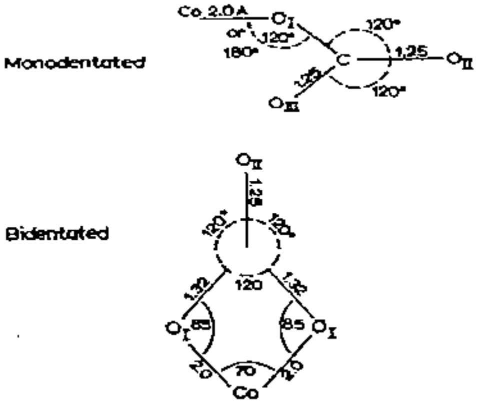


Fig. 2. Details of the structure of the carbonato ligand assumed[144].

There is excellent agreement between their selected parameters and the real values which are now known. (Compare pp. 190, 191.)

The frequencies which should appear in the IR spectra of CO$_3$$^{2-}$ containing compounds were calculated.

For the monodentate species, two possible symmetries were considered whilst only one was considered for the bidentate case.

Table 7 shows the results of their calculations.

TABLE 7

CALCULATED CO_3^{2-} LIGAND I R FREQUENCIES

Symmetry	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7	ν_8
monodentate $\nu_{cm^{-1}}$ *calc.* CO_3–*Co*								
C_s	1373	1039	765	369	1483	711	82	—
C_{2v}	1376	1069	772	303	1482	676	92	—
assignment								
	$(C–O_{II})$ $+(C–O_I)$ stretch	$(C–O_I)$ $+(C–O_{II})$ stretch	$(O_{II}–CO_{III})$ bend	$(C–O_I)$ stretch	$(C–O_{II})$ stretch	$(O_{II}CO_{II})$ rock		(CoO_ICO) bend
bidentate $\nu_{cm^{-1}}$ *calc.* CO_3–*Co*								
C_{2v}	1595	1038	771	370	1282	669		429
	$(C–O_{II})$ stretch	$(C–O_I)$ stretch	$(Co–O_I)$ stretch +ring def.	$(C–O_I)$ stretch +ring def.	$(C–O_I)$ stretch $+(O_ICO_{II})$ bend	(O_ICO_{II}) bend $+(C–O)$ stretch $+(C–O_I)$ stretch		(CoO_I) stretch

TABLE 8

EXPERIMENTAL IR FREQUENCIES

	Frequencies						
$[Co(NH_3)_5CO_3]NO_3$aq.	(1365)	(1052)	738	351	1482	690	854
$[Co(NH_3)_5CO_3]Br$	1373	1070	756	362	1453	678	850
$[Co(NH_3)_4CO_3]Cl$	1393	1030	760	395	1265	673	834
$[Co(NH_3)_4CO_3]ClO_4$	1632	—	762	392	1284	672	836

Note: all frequencies in cm^{-1}. Parentheses mean overlapped frequency.

These calculated frequencies were compared with the experimental values for many derivatives and showed a fairly good agreement.

Table 8 gives some of the experimental values. Deuteration has been used in some cases for verification.

The selection of C_s or C_{2v} symmetry for monodentate derivatives was determined by the agreement of ν_4 with experiment; C_s symmetry seems favoured.

Changes in the value of the force constants provides some interesting further information (Fig. 3).

These figures indicate that the equivalence of the three oxygen bonds of the

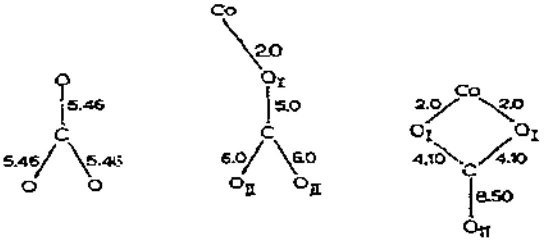


Fig. 3. Force constants; (dynes/cm).

free carbonato ion is lost upon coordination, the C–O$_{I}$ bond becoming weaker and C–O$_{II}$ becoming stronger. The absolute values of the force constants indicate rather strong coordinate bonds. Nomenclature and assignments from Fujita *et al*[144] shows some difference with Gatehouse *et al.*[140].

This type of work, using normal coordinate analysis for the calculation of IR spectra, has been carried out for some other cases, *e.g.* oxalato and sulfate ammino (of monodentate and bidentate character) Co^{III} complexes.

In the course of work dealing mainly with sulfato derivatives, Tanaka, Suyi and Fujita[146] also refer to carbonato pentammino Co^{III} including both calculated and observed data. Five frequencies and force constants are tabulated being slightly different from those reported here[144].

The spectral range extends to KBr and CsBr zones, *e.g.*

$[Co(NH_3)_5CO_3]Cl$ ν_{cm}^{-1} 510 495 470 358 330 290

The authors discuss the applicability of the Urey-Bradley method for the calculation of force constants and mention several factors as being possibly responsible for the differences observed: 1) C–O coupling; 2) H bridge formation; 3) molecular dimensions; 4) non-localized π bonds.

Regarding the type of bond, the authors consider it highly covalent.

Elliot and Hathaway[147] analyzed the assignments of Gatehouse and Fujita and in order to visualize the differences they drew diagrams showing the separation of ν_3 and ν_4 according to the two authors (Fig. 4).

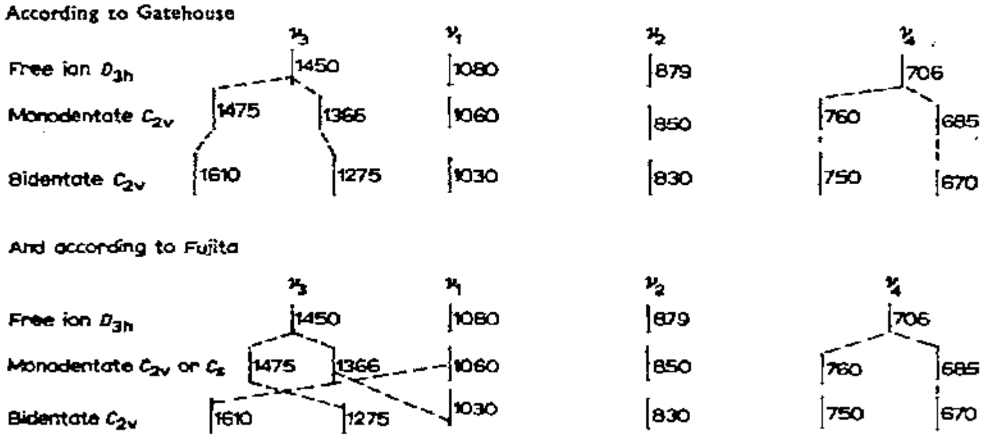


Fig. 4. Effect of lower symmetry on the vibrations of a carbonate group.

Both assignments correspond to the same experimental results. It is interesting that from this observation, an experimental method to distinguish mono from bidentated carbonate group evolves. The bidentate group will show a wider separation (1610–1275) in its high frequency absorption than the monodentate species (1475–1366 cm^{-1}).

Regarding the existence of C_s or C_{2v} symmetry in carbonato pentammino Co^{III}, considered by Fujita *et al.*[144] Elliot and Hathaway[147] report further information. Their work consists in obtaining an IR spectrum using IR polarized light focused on a single crystal oriented according to its axes. Allowed and forbidden frequencies can be calculated and the results compared with experimental data. In order to make such a calculation it is necessary to know the crystal structure and the authors used Barclay and Hoskins[115] results for $[Co(NH_3)_4CO_3]Br$. They oriented the 001 face and the spectra obtained shows 4 of the 6 bands calculated on consideration of C_{2v} symmetry for the CO_3 group. At that time, Elliot and Hathaway[147] pointed out that it would be interesting to carry out the same work for $[Co(NH_3)_5CO_3]X$ but the structure of these derivatives was still unknown (1965). The method will be able to show the type of symmetry, thus distinguishing C_s from C_{2v}.

As a matter of fact the X-Ray analysis was reported in the same year[145] for $[Co(NH_3)_5CO_3]Br$ and the work suggested becomes feasible. However the detailed structural knowledge resolves the question about the type of symmetry because the $M–O–CO_2$ angle is 137°, indicating C_s symmetry.

However, academic interest in the polarized IR spectra of an oriented crystal is maintained.

The IR spectrum of $Co[Co(CO_3)_3]$ was reported by Duval and Lecompte[148], by depositing its powder over NaCl.

J. Lapscombe[141] found different values using a KBr disc, for the complex $K_3[Co(CO_3)_3]3H_2O$. Decomposition of the complex was proven by the appearance of absorption peaks corresponding to $KHCO_3$ in a partially decomposed sample.

Comparison of the spectrum of the pure substance with other compounds led J. Lapscombe to the conclusion that the compound contained a monodentate carbonate group, supporting the formula $[Co(CO_3)_3(H_2O)_3]^{3-}$. This conclusion is considered erroneous as we will discuss later (section F).

As far as we know, no further work on the IR Spectra of $[Co(CO_3)_3]^{2-}$ compounds has been done. The spectral assignments for $CO_3{}^{2-}$ bridged frequencies[15] in $[Co_2(NH_3)_{10}CO_3]^{4+}$ suggest the presence of monodentate $CO_3{}^{2-}$.

(iii) *Magnetic properties*

The magnetic moment of the spin paired hexacoordinated cobalt(III) ion will not be far from zero, since all the electrons are paired. Nevertheless interest in the magnetic properties of many ammino derivatives of Co^{III} has grown as a result of ligand field theory implications[92,95,96,98].

The experimental values given by Kanekar and Nipankar[92] who studied 14 cobalt(III) ammine derivatives are, for the carbonato cases:

	$\chi a \times 10^6$	$\chi M \times 10^6$ cgs
$[Co(NH_3)_5CO_3]NO_3$	-0.017	-28.5
$[Co(NH_3)_4CO_3]NO_3$	$+0.070$	$+18.7$

We have found the same values for the pentammine derivative. The additivity of diamagnetism can be used to understand these figures.

The Co^{3+} ion has a very small positive susceptibility due to the second order temperature independent Zeeman effect (t.i.p.). Griffith and Orgel[93] were able to calculate this second order paramagnetism of Co^{III} ion for different ligand fields. Only the ${}^1T_{1g}$ state contributes and the following relationship holds:

$$\chi_{t.i.p.} = \frac{2N}{3}\left(\frac{e\hbar}{2mc}\right)^2 \frac{24}{E} = \frac{4{,}085}{K}$$

Where E and K are the Dq values in cycles per seconds or cm^{-1}, respectively. If we insert the 10 Dq values found previously, we arrive at 186×10^{-6} cgs/mol and 194×10^{-6} cgs/mol for the calculated molar paramagnetic contribution of the Co atom in the pentammino and tetrammino derivatives respectively.

On the other hand, from the experimental data and using Pascal constants we find the following values:

$[Co(NH_3)_5CO_3]NO_3 0.5H_2O$

$\alpha_{Co} = -28.5 + (5 \times 17.1 + 29.5 + 18.9 + 13) = 118.4 \times 10^{-6}$ cgs/mol.

which is far from the calculated value of 186×10^{-6} cgs/mol.

$[Co(NH_3)_4CO_3]NO_3 0.5H_2O$

$\alpha_{Co} = +18.7 + (4 \times 17.1 + 29.5 + 18.9 + 6.5) = +142.0 \times 10^{-6}$ cgs/mol.

which can be compared with the calculated value of 194.

The agreement is not good although the results are correctly ordered. The principal reasons for this disagreement are the uncertainty of Pascal constants and the errors in measurement. Usually it is very difficult[82] to get anything better then $\pm 25 \times 10^{-6}$ cgs/mol. The difference between chelated and non-chelated CO_3^{2-} ligand ought to have been considered but was not.

We have not recorded any other susceptibility measurement of these compounds.

The chemical shifts in the NMR spectra were reported[94] for $[Co(NH_3)_5CO_3]NO_3$ and $[Co(NH_3)_4CO_3]NO_3$ and the values agree with the calculated 2nd order paramagnetism.

(iv) *Polarographic behavior*

The D.M.E. (Dropping Mercury Electrode) reduction, as with most Co^{III} complexes, shows a two-wave polarogram corresponding to the processes

$[Co^{III}L_6] \rightarrow [Co^{II}L_6]$ and $[Co^{II}L_6] \rightarrow Co^0 + L$.

Since the second reduction step consumes $2e^-$ and the first only $1e^-$, the diffusion current ratio will be 2:1.

Tsuchida and coworkers[149] studied a series of acido-pentammino derivatives. The general scheme for reduction is:

$$[Co^{III}(NH_3)_5X]^{n+} + e^- \rightarrow [Co^{II}(NH_3)_5X]^{(n-1)+}$$

$$[Co^{II}(NH_3)_5X]^{(n-1)+} + H_2O \overset{\text{fast}}{\rightarrow} [Co^{II}(H_2O)_6]^{2+} + 5NH_3 + X^{(3-n)-}$$

$$[Co(H_2O)_6]^{2+} + 2e^- \rightarrow Co^0 + 6H_2O$$

which applies to carbonato and bicarbonato pentammino Co^{III}. The data are given in Table 9.

TABLE 9

	Supporting electrolyte		Supporting electrolyte	
	0.1 F K Cl		0.5 F K_2SO_4	
	1st wave $Co^{III} \rightarrow Co^{II}$	*2nd wave* $Co^{II} \rightarrow Co^0$	*1st wave*	*2nd wave*
$[Co(NH_3)_5CO_3]NO_3$	−0.38	−1.25	−0.50	max. value
$[Co(NH_3)_5HCO_3]NO_3$	—	—	−0.50	−1.28

Some acido pentammino Co^{III} present an additional wave, known as an "extrawave". Carbonato derivatives do not.

The polarographic stability in a series of compounds depends upon the substituting ligand. Regarding this series, carbonato and bicarbonato acido pentammine are situated at the end. The order is: I^-, Br^-, Cl^-, CrO_4^{2-}, $NCS^- < NO_3^- < N_3^- < SO_4^{2-} < NO_2^- < CrO_4^{2-} < Ac^- < NH_3 < H_2O < CO_3^{2-} < HCO_3^-$, which is different from the spectrochemical series. When the supporting electrolyte is changed, the position of the CO_3^{2-} and H_2O ligands is reversed.

In another report on carboxylato ammines of Co^{III} Yanagi and Kuroda[150] compared the polarograms of methanoic, ethanoic, propanoic, mono, di and trichloro acetic derivatives. The second wave is common to all of them and the first becomes more negative according to the following order of ligand: methanoic > monochloroacetic > dichloroacetic trichloroacetic, propanioc, which coincides with decreasing order of basicity. In other words, the polarographic stability decreases when the basicity of substituent ligand increases.

With reference to the carbonato tetrammine derivative, Fedorovich and Frumkin[151] reported the reduction in 0.1N KCl, producing 2 normal waves.

At higher dilution of the supporting electrolyte a dip appears in the diffusion current part of the wave which can be eliminated by adding a small amount of $BaCl_2$ or $[(C_2H_5)_4N]^+$ salt.

The existence of this type of anomalous behavior has been attributed in the past to the formation of a film of hydroxy-compounds over the DME. Addition of HCl normalizes the wave shape. This explanation is not correct for $[Co(NH_3)_4$-

$CO_3]^+$ because acid addition does not affect dip formation. Absorption phenomena at the electrode surface have been suggested as responsible in this case.

Carunchio and Campanella[152] studied the compounds $[Co(en)_2O_2CR]^+$ (R = Methyl, phenyl or cyclohexyl) whose polarograms show 2 or 3 waves assigned to the complex itself and coexistent aquocarboxylato and hydroxocarboxylato species.

Peuripoy and Schrenk[153] compared the results from several complexes including $[Co(NH_3)_4CO_3]^+$, obtained by means of SME (Stationary Mercury Electrode). The diffusion currents are 2 or 4 times those obtained from DME and $E_{\frac{1}{2}}$ becomes more negative.

R. Ralea *et al.*[34,124], (see page 167), also describe the classical and oscillopolarographic behavior of $[Co(NH_3)_4CO_3]^+$ ions in solution.

(v) *Thermal decomposition*

Thermal decomposition techniques have undergone a substantial improvement during the last 15 years. TGA (Thermo gravimetric analysis) and DTA (Differential thermal analysis) have demonstrated their importance in coordination chemistry and the method becomes more generally used.

In 1958 Wendlandt[154] studied a group of complex ammines including $[Co(NH_3)_4CO_3]NO_3 \cdot 0.5H_2O$ tabulating the initial decomposition temperatures and the "oxide point". The complex $[Co(NH_3)_4CO_3]NO_3 0.5H_2O$ begins to lose weight at 40° and converts into the oxide from 225° up.

A more detailed study was reported by Wendlandt *et al.*[52] comparing the

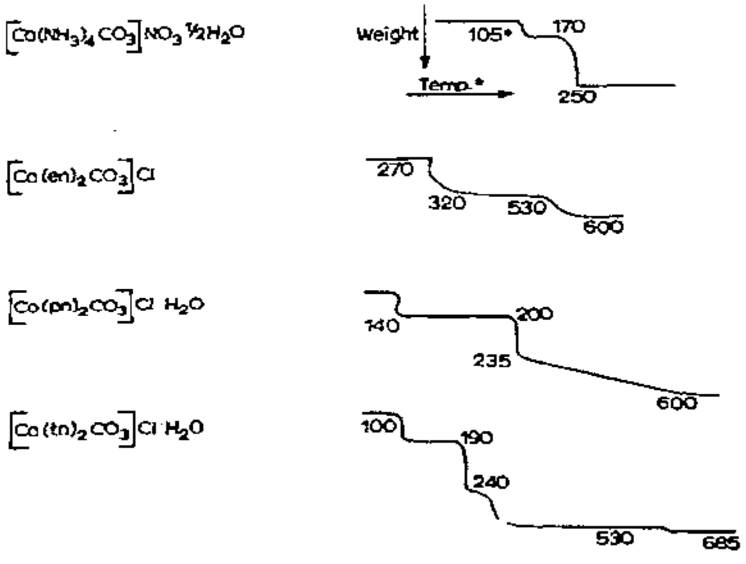


Fig. 5. Thermogravimetric data.

behavior of some carbonato derivatives of the tetrammine series: $[CoL_4CO_3]^+$ (L = NH_3, en, pn, tn). The oxalato complexes were also included.

Fig. 5 shows the approximate curve shape and characteristic points for TGA.

In all cases, elimination of water occurs at temperatures around 100°. The propylenediamine derivatives lose water at a slightly higher temperature, and all compounds produce anhydrous species.

Decomposition begins as low as 170° for the ammino derivative and at higher temperatures for the rest.

The final decomposition is said to produce Co_3O_4 probably with some contamination with other oxides. This oxide formation requires temperatures of the order of 600° except for the tetrammino which will explode at 250°.

DTA curves show endothermal peaks for

$[Co(tn)_2CO_3]Cl \cdot H_2O$ at 240°

$[Co(en)_2CO_3]Cl \cdot H_2O$ at 300°

and

$[Co(pn)_2CO_3]Cl \cdot H_2O$ at 255°

corresponding to complex decomposition.

On the other hand, the complex $[Co(NH_3)_4CO_3]NO_3 \cdot 0.5H_2O$ produces a very sharp endothermic peak and shortly after an exothermic one at 240° and 250° respectively.

All DTA curves show endothermic inflexions due to dehydration at the beginning (somewhere from room temperature to 200°).

Wendlandt and Woodlock[51] provided further information on $[Co(NH_3)_4CO_3]X$, X = Cl^-, Br^-, I^-, and NO_3^- specifying the decomposition products. The gaseous evolution is swept out with a stream of nitrogen, NH_3 is absorbed on 4% boric acid and titrated, and CO_2 is absorbed on "Ascarite" and weighed.

All compounds decompose predominantly according to:

$$6[Co(NH_3)_4CO_3]X(s) \rightarrow 3\,Co_2OX_2(s) + N_2(g) + 6CO_2(g) + 22NH_3(g) + 3H_2O(g)$$

The nature of the formulated Co_2OX_2 compound is unknown, but at 500° it becomes Co_3O_4. A somewhat different pattern should exist for bromide and nitrate, because the stoichiometry does not adjust perfectly. Iodine vapors have been detected in the case of the iodide.

Regarding the pentammino derivatives there is one report from Figlarz[50] who studied hydrogen atmosphere pyrolysis of complexes $[Co(NH_3)_5X]NO_3$ X = formiato, acetato, propionato and carbonato.

Explosive decomposition at between 185 and 205° yielding oxides or Co^0 at higher temperatures was found. The $[Co(NH_3)_5CO_3]NO_3H_2O$ complex produces CoO at 185° and Co^0 at 220–300°.

The TGA curves for: $K_3[Co(NO_2)_2(CO_3)_2]2H_2O$; $[Co(NH_3)_6][Co(NO_2)_2(CO_3)_2]2H_2O$; $[Co(NH_3)_6][Co(NO_2)_2(CO_3)_2]$; $K_8[Co_2(NO_2)_8(CO_3)_3]2H_2O$; $K_8[Co_2(NO_2)_8(CO_3)_3]$ are reported by Golovnya *et al.*[24].

(vi) *Other properties*

Refraction index—In the course of a general study of a method relating the additivity of refraction indices with structural parameters, Bokii and Batsanov[155] included the compounds:

$[Co(NH_3)_4CO_3]_2SO_4 3H_2O \qquad R_m = 86.42$

$[Co(NH_3)_4CO_3]_2SO_4 \qquad R_m = 76.73$

assigning the difference to the water molecules, $\Delta R_{H_2O} = 3.23$. This value is very close to the normal crystallization value $\Delta R_{H_2O} = 3.26$ found in other well-known cases and rather distinct from the value corresponding to hydrogen bonded water *e.g.* ice $\Delta R_{H_2O} = 3.58$.

These results support the idea that the water molecules in such crystals are not hydrogen bonded; therefore they must be considered as crystallization water.

Ionic mobility.—Jander, Blohm and Gruttner[156] compared the specific diffusion coefficients and the mobilities of a series of ions. The regularities found between these magnitudes suggested the calculation of mobility as an empirical function of diffusion coefficient. The calculation for $[Co(NH_3)_4CO_3]^+$ gave 60.7 Ω^{-1}millimol^{-1}; 63 Ω^{-1}millimol^{-1} is the experimental value from direct conductance measurements.

NMR spectra.—The chemical shifts of many complexes have been reported by Dharmatti, Kanekar and Mathur[157]. $[Co(NH_3)_4CO_3]^+$ and $[Co(NH_3)_5CO_3]^+$ are included. The chemical shifts are ordered according to the magnetic screening ability of each substituent ligand. The following order is obtained:

ac.ac. $<$ oxine $<$ bidentate CO_3^{2-} $<$ Cl^- $<$ monodentate CO_3^{2-} $<$ H_2O $<$ $<NH_3$ $<$ en $<$ dipy $<$ CN^-.

Clifton and Pratt[158] reported that the presence of a substituting group produces a discrimination among the ammonia ligands according to the *cis* or *trans* position.

The hexammino Co^{III} derivatives show a peak at 134 cycles/sec and the carbonato derivatives show two:

$[Co(NH_3)_5CO_3]^+$	91 cycles/sec and 144 cycles/sec.
$[Co(NH_3)_4CO_3]^+$	112 cycles/sec and 138 cycles/sec.

Heat capacity at low temperatures.—Jensen and Beevers[159] have found that $[Co(NH_3)_4CO_3]NO_3$ does not show a λ transformation between -180 and $+20°$

Radiation effects. Prakash *et al.*[160]. reported on the effect of high amplitude sound waves on $[Co(NH_3)_4CO_3]NO_3 \cdot 0.5H_2O$. The degradation of the complex is assigned to the effect of free radicals formed in the aqueous solution (H, OH and O_2H) in a solvolytic process.

Photo-decomposition of various pentammines, including $[Co(NH_3)_5CO_3]^+$, has been studied[161] in the concentration range 10^{-2}–10^{-4}M. The Co^{II} formation rate depends on pH, going down as pH goes up. Maximum effect occurs at pH 4–5.

The Szilard Chalmers Recoil was also studied for some carbonato complexes, *e.g.* Lazzarini[162].

Characteristic microchemical reactions.—Crystalline characteristic precipitates[163] are produced by $[Co(NH_3)_4CO_3]^+$ with HF_2^- and BrO_3^-.

Basic strength.—Lamb and Yngve[164] obtained hydroxides from complex cations using hydrated silver oxide.

For solutions of $[Co(NH_3)_4CO_3]OH$ the conductivity is highest showing 97% dissociation.

Hydrogen–deuterium interchange.—Carbonato ammino co^{III} complexes show the same features as other ammines of Co^{III}. All hydrogen atoms behave equally with respect to deuterium exchange[165]. Nevertheless Bankowski had reported[166] previously that $[Co(NH_3)_4CO_3]Cl$ has only three exchangeable hydrogen atoms.

In 1937, James, Anderson and Briscoe[167] corrected this conclusion, reporting a very slow exchange rate compared with other ammines ($T_{\frac{1}{2}}$ several hours at 25°–30 °C).

H–D exchange velocity measurements for several cobalt(III) ammines have been reported, *e.g.* Block and Gold[168] and a table summarizing most of the known values is inserted in Basolo and Pearson's book[169], but the carbonato ammino complexes of Co^{III} are not listed.

F. MONO AND BIDENTATE CHARACTER OF THE CARBONATE LIGAND

Acknowledgement of the existence of Co^{III} carbonato ammines having monodentate and bidentate CO_3^{2-} groups, led to misleading interpretations in the old literature.

In 1903, Werner[170] studied $[Co(NH_3)_4CO_3]NO_3 0.5H_2O$ and $[Co(NH_3)_5CO_3]NO_3 \cdot H_2O$ and suggested the presence of bi and monodentate carbonato ligand, respectively; some time later[171] taking into consideration the impossibility of dehydration even at temperatures higher than 120° and the alkalinity of aqueous solution he reconsidered the problem, suggesting the pentammino derivative to be an intramolecular salt

$$[(NH_3)_5CoOCO_2H]OH \cdot X$$

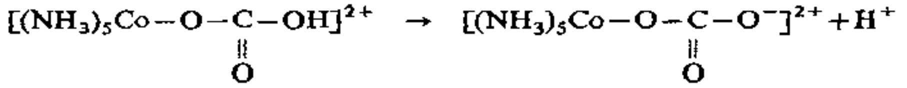
giving structural significance to the water molecule. By analogy with the betaine formula used for glycine and other amino acids, he called this a "betoxine salt".

Matsuno[172] considered the possibility that the water molecule of $[Co(NH_3)_5CO_3]NO_3 \cdot H_2O$ could be coordinated water with the CO_3^{2-} group remaining bidentate resulting in an octocoordinated cobalt complex $[Co(NH_3)_5CO_3H_2O]^+$ and he claimed to have resolved optical isomers. Duval[173] was unable to repeat this resolution and obtained different analytical results. He also pointed out that several salts of this cation may be anhydrous, at least in the solid state. (PO_4^{2-}, SO_4^{2-}, $C_2O_4^{2-}$). After that, the original Werner formula was maintained. Afterwards, Lamb and Mysels were able to dehydrate the complex $[Co(NH_3)_3CO_3]NO_3 \cdot 1H_2O$ by a special technique and this is considered as a final check of the non-structural significance of the water molecule in the solid[a,b].

Another idea gave birth to different considerations. The monodentate character of CO_3^{2-} in pentammino Co^{III} compounds, involves one Co–O bond, allowing the rest of CO_3^{2-} group to orient itself[174,175]. This structural feature was first mentioned by J. C. Duff[100].

On this basis, using 1945 bonding ideas, it was said[31] that the CO_3^{2-} group was covalently bonded to Co through one oxygen atom. Water, due to its dielectric properties, enhances the electrostatic character of oxygen atoms which are not coordinated to Co^{III}.

The resulting dipolarity of complex ions has given rise to the use of the term "zwitter-ion" applied originally to some organic compounds such as certain amino acids, *e.g.* glycine. This zwitterion character of the complex can be looked upon as:



$$[(NH_3)_5Co-O-\underset{\underset{O}{\|}}{C}-OH]^{2+} \rightarrow [(NH_3)_5Co-O-\underset{\underset{O}{\|}}{C}-O^-]^{2+}+H^+$$

These ideas should be considered as related historically with reference to the conclusions we mentioned before, regarding protonation and deprotonation involved in hydrolytic processes.

Previously, Pfeiffer[176] studied $C_2O_4^{2-}$ and CO_3^{2-} as ligands capable of using 1 or 2 coordination sites and he mentioned the relationship between the charge of the ion and its ability for monodentate or bidentate coordination. In the $C_2O_4^{2-}$ monodendate ligand he also considered the formation of a zwitterion according to protonation and deprotonation of the ligand in the complex.

A direct experimental test showing the different behavior of monodentate and bidentate CO_3^{2-} ligand was presented by Lamb and Mysels[31] who measured the molar dielectric increment for $[Co(NH_3)_5CO_3]NO_3$ and $[Co(NH_3)_4CO_3]NO_3$ in glycol solution, finding a ratio of two for the pentammino/tetrammino figures.

On the other hand the acceptance of CO_3^{2-} as a bidentate ligand has also been a matter of some discussion.

---

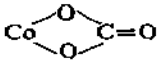
[a] Some different water content of 0.5M has been reported[32,197] for the $[Co(NH_3)_4CO_3]NO_3$.

[b] We tried Carl Fisher reagent without significant results[34].

A four-atom ring chelate has been recognized as unstable and rare; as late as 1960, Schwarzenbach[177] includes CO_3^{2-} in a classification of chelating agents, under the heading: "precipitant ion producing polynuclear structures". He emphasized that the impossibility of this ion to form more than one bond with a central atom is related to the strain in the ring so formed. Evidently, this statement does not refer to the complexes we are reviewing.

We mentioned above the problem concerning the nature of the CO_3^{2-} bond in the ion $Co(CO_3)_3^{3-}$.

The two alkaline salts of this anion crystallize as three-hydrates and it has not been possible to dry this water off without decomposition. This information together with the IR spectra (see page 181) and the abnormally high strain that $(CO_3^{2-})_3$ bidentate groups ought to produce, (a 70° angle is known for one

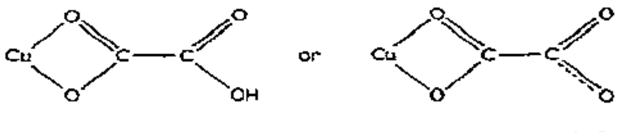


group in a Co^{III} regular octahedral complex) are the principal reasons for the suggested formulae $[Co(CO_3)_3(H_2O)_3]^{2-}$ or $[Co(CO_3H^-)_3(OH)_3]^{2-}$. Furthermore, other facts, such as stability conditions, (highly concentrated $KHCO_3$ solution) and the experimental failure to resolve optical isomers also agree with such formulae. Nevertheless the preparation of some anhydrous derivatives, (see page 151) and the analogy with the much better studied trioxalato series, are good arguments favoring the trichelate formula.

The important synthetic work using $Co(CO_3)_3^{3-}$ as a starting material can also be looked upon as supporting argument for the tris-carbonato cobaltate ion formula.

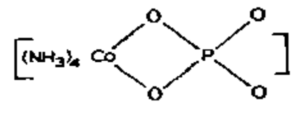
Furthermore, the four-atom ring formation has proved to be not so exceptional. Complexes of group III, IV and actinides do exhibit better stability for 4-atom chelates than for 5-atom rings. This has been considered a case of inversion of the Chugaev rules.

Also, as Zaitsev points out[178], there are some oxalato complexes where the 4-atom ring is formed, *e.g.* $(NH_4)_2Cu(C_2O_4)_2 2H_2O$ having two O–O distances 2.65 and 2.27 Å, with the structure:



and some other examples such as $(NH_4)_4[Zr(C_2O_4)_4]$ and $Ba_2[Zr(C_2O_4)_4]$, etc.

Furthermore bidentate phosphates obtained by using carbonato derivatives as a starting material, display the 4 atom ring[22], *e.g.*



The X-Ray Diffraction method of structural resolution was applied to $[Co(NH_3)_4CO_3]Br$ in 1962[115], and for $[Co(NH_3)_5CO_3]Br$ in 1965[145] and as usual, this powerful direct method definitely answered most of the remaining questions.

Barclay and Hoskins reported the crystalline and absolute structure resolution of $[Co(NH_3)_4CO_3]Br$ giving the following information: orthorhombic: $a = 6.760$ Å $b = 7.629$ Å $c = 16.886$ Å $v = 870.8$ Å^3 Dm $= 2.028$ g · cm^{-3} (flotation) $z = 4$ spacial group Pzcmn.

The crystalline structure consists of layers of complex ions with bromide ions in between. Br–N distances vary from 3.50 to 3.84 Å suggesting the presence of hydrogen bonds.

The CO_3^{2-}–Co bonding structural details are given in Fig. 6.

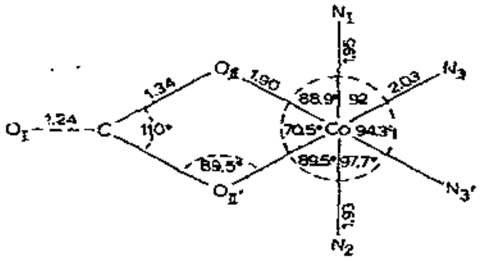


Fig. 6. X-Ray structure of $[Co(NH_3)_4CO_3]^+$ ion.

The small oxygen–cobalt oxygen 70° angle suggests an important molecular strain. The smaller distance of O_I–C justifies the double bond contribution.

The CO_3^{2-} ligand exerts some *trans* effect over the $N_{3\,3}'$ atoms modifying the N–M–N angles.

Some previous crystallographic work was known. Goniometric measurements were performed by Strock and McCutcheon[179], Strock[180] and Flint[181].

In 1963, Hagensen and Rasmussen[182] discussed the Barclay and Hoskins results, comparing data with their own. They were working on the same structure and no important disagreements were reported.

Also in 1962, A. Amit and coworkers at my request did preliminary work, still unpublished, with $[Co(NH_3)_4CO_3]NO_3 0.5H_2O$ and $[Co(NH_3)_5CO_3]NO_3 \cdot H_2O$.

Freeman and Robinson[145] in 1965 resolved the structure of $[Co(NH_3)_5CO_3]$-$Br \cdot H_2O$

orthorhombic: $a = 12.37_0$ Å $b = 12.14_4$ Å $c = 6.43_3$ Å

Spacial group Pna21

There is an octahedrally coordinated monodentate carbonato ligand, with one Co–O bond, $d = 1{,}99$ Å, and five Co–N bonds, $d = 1.94, 1.93$ Å.

The bromide ion forms a bridge between NH_3 and H_2O.

The CO_3^{2-}–Co detail is given in Figure 7.

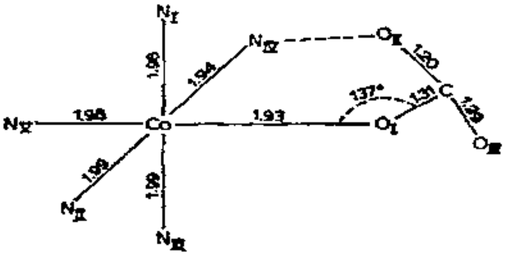


Fig. 7. X-Ray structure of $[Co(NH_3)_5CO_3]^+$ ion.

There are hydrogen bonds between $O_{(II)}$ and $N_{(IV)}$. A triple *trans*-effect is observed from CO_3^{2-} to $N_{(I,\,II,\,V)}$. The $[Co(NH_3)_5CO_3]NO_3 \cdot H_2O$ complex has been reported to adopt two possible crystalline forms, as needles or rectangular plates, according to whether it is crystallized from strongly ammoniacal solution or from water.

Recently the absolute structure resolution of $[Co(NO_2)_2(NH_3)_2CO_3]^-_4$ was reported[183] (see section G).

The bridged CO_3^{2-} is represented by three compounds and no structural studies have been reported.

Bonding.—The Co^{III}–O bond in hexacoordinated complexes will show features dependent upon electronic behavior of the oxygen atom. The oxygen atom can form, ionic, or covalent, σ bonds, and donor π bonds[184] with metals; if the differences in electronegativity between oxygen and the bonding atom are not too big and the central atom, has d or f orbitals available the bonds are usually σ covalent with a strong π contribution.

The force constants for the Co–O bond from IR spectroscopy have been mentioned before. In the monodentate complexes the bond should be mostly σ but in bidentate complexes there is an important contribution to the stability from π bonding.

The C–O_{II} distances for bidentate coordination is 1.34 Å and for monodentate coordination C–O_I is 1.31 Å both showing mean values between $d_{C-O} = 1.43$ and $d_{C=O} = 1.21$ Å.

G. STEREOISOMERISM

Interesting cases of *cis-trans* and optical isomerism are found among these complexes and some of them have been studied.

The $(NH_4)[Co(NH_3)_3C_2O_4CO_3]$ complex can be facial or meridianal as far as the NH_3 ligands are concerned. The compound is obtained using trioxalato cobaltate salt as a starting material but this fact does not permit us to predict which isomer will result from the reactions involved.

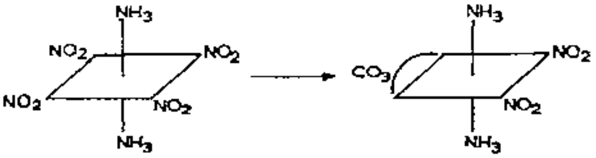
The $[Co(NH_3)_4NO_2CO_3H]X$ complex is probably the *trans* isomer because it is obtained by passing a stream of CO_2 over $[Co(NH_3)_4NO_2OH]NO_3$ which will surely be *trans* due to the *trans* effect of NO_2. Nevertheless this has not been proved or studied.

The $(NH_4)\,[Co(NH_3)_4(CO_3)_2]$ complex can also be presumed to be *trans* for the same reasons; but again it has not been proved.

The dicarboxylic acid derivatives $[Co(NH_3)_4(RCO_2)_2]^+$ and also $[Co(en)_2(RCO_2)_2]^+$ show *cis-trans* isomerism which has been studied in many cases.

The mixed types $M[Co(NH_3)_2(NO_2)_2CO_3]$ are prepared using the Erdman type salt $NH_4[Co(NH_3)_2(NO_2)_4]$ reacting with a saturated solution of $KHCO_3$ at 60–70 °C. Only two NO_2 ligands are replaced by one $CO_3{}^{2-}$ and the resultant compound has the $2NH_3$ in *trans* position. The possibility of asymmetric substitution has no part in the reaction.

The *trans* effect of NO_2 ligand combined with the *trans* positioning NH_3 ligands explains the reaction course[11,13]:



X-Ray diffraction structural work for $K[Co(NH_3)_2(NO_2)_2CO_3]2H_2O$ has been carried out by Butman, Alsanov and Porai Koshits[183] and the results confirm all previous deductions.

The $[Co(NH_3)_2enCO_3]Cl$ complex was originally prepared by Werner[185] and in 1940, Bailar and Peppard were able to obtain both *cis* and *trans* isomers[186]. The *cis*-$[Co(NH_3)_2enCO_3]^+$ complex is obtained by reaction of [Co *trans* Br_2 *cis* $(NH_3)_2en]^+$ with Ag_2CO_3. The evidence for the *cis* isomer produced is the optical activity. The *trans* $[Co(NH_3)_2enCO_3]Cl$ complex is obtained using [Co *cis* Cl_2 *trans*$(NH_3)_2en]Cl$.

The $K_2[Co(NH_3)\,(NO_2)_3CO_3]$ derivative could have facial or meridianal NO_2 groups. It has been possible to deduce that the compound is meridional because, if a solution of $[Co(NH_3)\,(NO_2)_3CO_3]^{2-}$ in concentrated ammonia is treated with glacial acetic acid it crystallizes on cooling into *mer* $[Co(NH_3)_3(NO_2)_3]$ and not the facial isomer, or a mixture.

One of the better known cases of *cis-trans* isomerism in this series is that of the *cis* and *trans* $K[Co(NH_3)_2(CO_3)_2]$, being blue and violet respectively. The visible spectra for both have been reported[21–23].

Archer and Catsikis[187] reported a study of the reaction of both isomers with acetyl-acetone. No matter whether the *cis* or *trans* compound is used, they always produce *cis* $[Co(acac)_2(NH_3)_2]^+$. This reaction involves a rearrangement when the starting material is the *trans* isomer.

Shibata, Mori and Kyuno[14] also found that *cis*-$[Co(CO_3)_2(NH_3)_2]^-$ transform to *trans*-$[Co(NO_2)_4(NH_3)_2]^-$. This is an interesting reaction for the study of the *trans* effect for hexacoordinated compounds.

Another important reaction involving a rearrangement is

$$[Co(CO_3)_3]^{2-} + 2KNO_2 \rightarrow trans[Co(NO_2)_2(CO_3)_2]^{2-} + K_2CO_3$$

studied by Golovnya *et al.*[24]. This reaction implies 2 ring openings. The *trans* effect of the NO_2 ligand controls the process.

Dinuclear compound formation will play an important role in the opening process. Under different conditions a one carbonato bridge compound of this formula $K_8[Co_2(NO_2)_8(CO_3)_3]$ is obtained[24].

Compounds that show possibilities of optical isomerism include:

1) *cis*$[Co\ en\ (NH_3)_2CO_3]Cl$ 2) *cis* $K[Co(NH_3)_2C_2O_4CO_3]$

3) $[Co(NN)_nCO_3]X$ NN = en, pn, tn, ptn, trien, dipy, phen, etc.

4) *cis* $K[Co(NH_3)_2(CO_3)_2]$ 5) $K[Co(en)(CO_3)_2]H_2O$

6) $M_3[Co(CO_3)_3]3H_2O$

Compound 1 has been partially resolved by Bailar and Peppard[186] using active quartz. As a matter of fact this partial resolution has been used for identification of the *cis*-isomer.

The complexes 3 show several examples of resolution and optical rotatory dispersion and circular dichroism studies have been carried out. Of these, the best known and most important are those of $[Co(en)_2CO_3]^+$, used for the famous Walden inversion studies[188,189].

The resolution of $[Co(pn)_2CO_3]CO_3$ [190] and $[Co(trien)CO_3]^+$ [191] has been also reported by Bailar's group.

The $[Co(en)_2CO_3]^+$ ion was used for resolution studies with active quartz[192] and using chromatographic starch columns[193].

This case of optical isomerism was thoroughly examined by T. Mathieu in his fundamental work on the optical rotatory dispersion of complexes[194]. Their O.R.D. curves were also investigated later by J. J. Bruschmiller *et al.*[195].

Dwyer and McDermont[196] reported methods of preparation for D and L $[Co(pn)_2CO_3]Cl \cdot H_2O$ and the O.R.D. curves are reported.

Derivatives under numbers 2, 4, 5 and 6 have not been resolved. The $[Co(CO_3)_3]^{2-}$ was not resolved despite the efforts of Mori, Shibata, Kyuno and Adachi[21]. They tried L-Strychnine and $d[Co(en)_3]^{3+}$ but probably due to chemical and kinetic instability the experimental work was unsuccessful.

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Abbreviations used in this paper:

en = ethylenediamine
pn = propylenediamine
ptn = diaminopentane
dipy = dipyridyl
phen = 1,10-phenanthroline
ata = nitrilotriacetate
edda = ethylenediaminediacetate
gly = glycine
L-ala = L-alanine
L-val = L-valine