

Tetrakis(pyridine)cobalt(III) Complexes

JOHAN SPRINGBORG^a and CLAUS ERIK SCHÄFFER^b

^a Department of General and Inorganic Chemistry, Royal Veterinary and Agricultural University, Thorvaldsensvej 40, DK-1871 Copenhagen V, Denmark and ^b Chemistry Department I (Inorganic Chemistry), University of Copenhagen, H. C. Ørsted Institute, Universitetsparken 5, DK-2100 Copenhagen Ø, Denmark

One of the isomers of carbonatochlorotris(pyridine)cobalt(III) has been prepared for the first time. It gives with pyridine the new carbonatotetrakis(pyridine)cobalt(III) ion, which with acid gives the new *trans*-diaquatetrakis(pyridine)cobalt(III) ion. These two ions have been isolated as their perchlorates. They both have extreme protolytic properties. The carbonate ion in strongly acid water solution protonates in two steps the first of which corresponds to an acidity constant (in 8 M sodium perchlorate) of 0.3 M. The acid decomposition of the carbonate ion to give carbon dioxide is unusually slow and results in the *trans*-diaqua ion whose first acidity constant (in 1 M sodium nitrate) is 0.04 M.

The only tetrakis(pyridine)cobalt(III) complex that has been reported¹ so far is the *trans*-dichloro ion. Among the other metals of the first transition period all the known tetrakis(pyridine) complexes also have the *trans*-structure. In Chemistry Department I several vain attempts have been made to prepare *cis*-complexes within the chromium(III) series.

On the other hand *cis*-complexes are not sterically impossible since they are known among the metals of the second^{2,3} and third⁴ transition metal series. However, here the greater radii of the ions, and the greater thermodynamic stability and particularly the greater robustness (inertness) of the complexes may be responsible for their apparently greater stereochemical liberalism.

With cobalt(III), as opposed to chromium(III), the carbonate ion is known^{5,6} to bind as a bidentate ligand. This property together with the carbonate ion's easy removal with acid, often under stereochemical retention of configuration, has made it widely used for preparing *cis*-complexes of the chromophoric type CoN_4O_2 within the amine and ammine series.

Also in the present paper the carbonate ion has been used, and carbonatochlorotris(pyridine)cobalt(III) has been prepared as an initial material for other pyridine-cobalt(III) complexes. Our aim was to prepare the carbonatotetrakis(pyridine)cobalt(III) ion and this aim has been reached. Our further

purpose, however, was to use this compound for preparing other *cis*-tetrakis(pyridine) complexes, which would be of spectroscopic interest. This purpose has not been achieved. By reaction with acid this carbonato complex gives the *trans*-diaqua ion, or with strong hydrochloric acid the *trans*-dichloro ion, and no evidence has been provided for the existence of *cis*-complexes, except the carbonato complex itself.

PREPARATIONS

An aqueous solution of the green tris(carbonato)cobalt(III) anion was prepared⁷ by addition of a solution of cobalt(II) chloride in dilute hydrogen peroxide to an excess of solid potassium hydrogencarbonate. This solution reacts with a mixture of pyridinium chloride and hydrochloric acid with formation of a blue-violet solution. The blue-violet colour is without doubt due to the replacement of coordinated carbonate ions by pyridine molecules. By evaporation of the reaction mixture at room temperature, carbonatochlorotris(pyridine)cobalt(III) is formed.

Evaporation at room temperature appeared to be essential. Upon standing at room temperature for two weeks without evaporation no precipitate was formed. Heating of the reaction mixture, on the other hand, caused rapid reduction to cobalt(II).

Some experiments in which nitrate was substituted for chloride were carried out. Nitrate, which generally is a weaker ligator than chloride, was used in an attempt to increase the number of pyridine molecules substituted, in order to obtain the carbonatotetrakis(pyridine)cobalt(III) ion directly from the tris(carbonato)cobalt(III) ion. However, no well-defined products were isolated from these mixtures.

Carbonatochlorotris(pyridine)cobalt(III) dissolves in pyridine with a violet colour. Heating of this solution causes complete reduction to cobalt(II). However, by addition of bis(pyridine)mercury(II) perchlorate to the cold solution and subsequent heating to 50°C, no substantial reduction to cobalt(II) occurs, and the chloride is replaced by pyridine yielding the red carbonatotetrakis(pyridine)cobalt(III) ion. This was isolated as the red perchlorate salt.

From the reaction of carbonatotetrakis(pyridine)cobalt(III) perchlorate with 12 M perchloric acid at room temperature, the brownish *trans*-diaquatetrakis(pyridine)cobalt(III) perchlorate was isolated.

EXPERIMENTAL

Materials. Pyridine, "chem. pure", was purchased from Riedel-de Haën, sodium perchlorate, "puriss. p.a.", from Fluka AG, Buchs SG, and sodium nitrate, "zur Analyse", from Merck. $[\text{Hgpy}_2](\text{ClO}_4)_2$ was prepared according to the literature.⁸ All other chemicals were of reagent grade and were used without further purification.

Spectra and identification methods. Absorption spectra in the 300–650 nm region, recorded using either a Cary Model 14 or a Zeiss DMR 21 spectrophotometer, were used as a check of purity and as characterization of the compounds. Data for maxima, minima, and shoulders have been given below as (ϵ, λ), the absorbancy ϵ in l/mol cm and the wavelength λ in nm.

Infrared spectra of the compounds in potassium bromide disks were recorded on a Perkin-Elmer 457 grating infrared spectrophotometer.

Powder X-ray diffraction diagrams were obtained using a Guinier powder camera with Cu-radiation.

pH-Measurements. The pH-measurements were made with a G 202 C glass electrode and a K 401 calomel electrode connected to a PHM 52 digital pH-meter, all from Radiometer, Copenhagen.

The pH-meter was adjusted to show $\text{pH} = 2.000 \pm 0.002$ in 0.01000 M HNO_3 , 1 M NaNO_3 . It is then assumed that the readings on the meter are equal to $\text{p}[\text{H}^+]$ in 1 M NaNO_3 solutions at 25°C.

Preparative procedures. Properties of and measurements on the individual compounds

1. *Carbonatochlorotris(pyridine)cobalt(III)*, $[\text{Copoly}_3\text{CO}_3\text{Cl}]$. A solution of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (119 g, 0.5 mol) in a mixture of water (2500 ml) and hydrogen peroxide (112 ml, 30 %) was portionwise and with stirring added to solid potassium hydrogencarbonate (750 g, 7.5 mol) in a 4 l beaker. The potassium hydrogencarbonate dissolved with a vigorous evolution of carbon dioxide gas and formation of a green solution of the tris(carbonato)cobaltate(III) ion. In order to complete the catalytic decomposition of the excess of hydrogen peroxide, the solution was allowed to stand for half an hour at room temperature. It was then cooled in an ice bath to about 5°C. An ice-cold mixture of pyridine (200 ml, 2.48 mol) and 12 M hydrochloric acid (580 ml, 6.96 mol) was then added dropwise to the stirred solution with continued cooling during one hour. Carbon dioxide gas was evolved and the colour of the solution turned from green to red-violet. The mixture was allowed to stand for another 2 h in the ice bath and was then left at room temperature in an open shallow dish. After about a week evaporation had reduced the volume to approximately 1200 ml.* Within two or three days the precipitation of blue-violet crystals of carbonatochlorotris(pyridine)cobalt(III) set in. Brownish by-products and some potassium chloride were also precipitated. The mixture was filtered, washed thoroughly with water and then with methanol (three 100 ml portions). By the washing most of the impurities were removed. Drying in the air yielded 85 g of blue-violet crystals of almost pure carbonatochlorotris(pyridine)cobalt(III) (43 %, based upon cobalt(II) chloride). (Found: Co 15.27; C 48.80; H 3.95; N 10.76; Cl 9.09. Calc. for $[\text{Copoly}_3\text{CO}_3\text{Cl}]$: Co 15.05; C 49.07; H 3.86; N 10.73; Cl, 9.05.) This product was used in the following synthesis. For further purification the almost pure carbonatochlorotris(pyridine)cobalt(III) (4 g) was dissolved in methanol (300 ml) at 50°C, filtered, and cooled in ice as quickly as possible. Small blue-violet needle-shaped crystals separated. After 3 h of cooling the sample was filtered and washed with ice-cold methanol (three 10 ml portions). Drying in air yielded 1.04 g (26 %). A check on the purity was made spectrophotometrically. (Found: Co 15.00; C 48.98; H 3.90; N 10.82; Cl 8.99.) (ϵ, λ)_{max}: (50, 577); (60, 409). Medium: 80 % v/v acetonitrile in water.**

Properties. Carbonatochlorotris(pyridine)cobalt(III) is sparingly soluble in water and methanol. In aqueous and methanolic solutions it is decomposed so rapidly that measurements of the visible absorption spectrum are difficult. The difficulties also arise from the slow rates at which the compound dissolves in these media. The visible absorption spectrum was therefore measured in 80 % v/v acetonitrile in water, as the compound dissolves readily in this medium. However, also in this medium the decomposition is fast. The colours of the solutions for the three media mentioned above are blue-green in daylight and violet in electric light.

* In one experiment with quantities scaled to 1/10 of those given above, the reaction mixture was evaporated at 35°C in a rotating vacuum evaporator within some hours. The yield of carbonatochlorotris(pyridine)cobalt(III) was only 1.05 g (5.3 %).

** The decomposition even in this medium is fast. In the extrapolation of the ϵ values at the maxima to the time of dissolution corrections up to 5 % were required, thus increasing the experimental error of the estimated ϵ values. A deviation within 2 % was found between the ϵ values of this sample and the sample recrystallized four times.

Carbonatochlorotris(pyridine)cobalt(III) reacts within minutes with either 4 M perchloric acid or 4 M hydrochloric acid, in both cases with evolution of carbon dioxide, but yielding different tris(pyridine)cobalt(III) complexes, which will be described in a forthcoming paper.

The infrared spectrum of carbonatochlorotris(pyridine)cobalt(III) was compared with that of trichlorotris(pyridine)cobalt(III) and showed clearly additional bands in the ν_1 (1675 (broad), 1640 (sharp) cm^{-1}) and ν_5 (1245 (sharp) cm^{-1}) regions ⁹ of the bidentately coordinated carbonate ion (see also p. 3318).

2. *Carbonatotetrakis(pyridine)cobalt(III) perchlorate*, $[\text{Copoly}_4\text{CO}_3]\text{ClO}_4 \cdot \text{H}_2\text{O}$. Bis(pyridine)mercury(II) perchlorate (7.5 g, 13.4 mmol) was added to cold pyridine (160 ml) in a 250 ml flask. The mercury(II) complex dissolved partly. Finely powdered, crude, but yet almost pure carbonatochlorotris(pyridine)cobalt(III) (10 g, 25.5 mmol) was then added. It dissolved partly, giving a violet colour. The flask was equipped with a calcium chloride tube and the mixture stirred under heating in a water bath at 50°C for 45 min. By this treatment all the solids dissolved and the colour changed to red. Cooling for half an hour in ice caused precipitation of red crystals of carbonatotetrakis(pyridine)cobalt(III) perchlorate. To complete the precipitation 200 ml of dry ether was added. The precipitate was filtered, washed with ether and dried in air. The crude product (13.5 g) was dissolved in water (1500 ml) at room temperature and a saturated water solution of sodium perchlorate (150 ml) was added to the filtered solution with stirring and cooling in ice. The precipitate was filtered and washed with ice-cold water (30 ml) and 96 % ethanol (two 30 ml portions). Drying in air yielded 8.4 g of the almost pure salt (60 % based on carbonatochlorotris(pyridine)cobalt(III)). 2.5 g of this salt was dissolved in water (280 ml) and a saturated water solution of sodium perchlorate (30 ml) was added to the filtered solution. The yield was 2.0 g (80 %). The sample reprecipitated twice was pure. (Found: Co 10.70; C 45.85; N 10.16; H 4.00; Cl 6.46. Calc. for $[\text{Copoly}_4\text{CO}_3]\text{ClO}_4 \cdot \text{H}_2\text{O}$: Co 10.66; C 45.62; N 10.14; H 4.01; Cl 6.41.) Visible spectra in different media are collected together in Table 2.

Properties. In contrast to carbonatochlorotris(pyridine)cobalt(III), the carbonatotetrakis(pyridine)cobalt(III) ion reacts extremely slowly with strong acids. So, the visible absorption spectrum in 1 M hydrochloric acid only changed very slowly at room temperature. Within a period of 2 h the positions of the maxima and minima remained constant and the changes in the ϵ values were less than 1 %. Contrary to this the visible absorption spectrum in 1 M HCl, 6 M LiCl changes much more rapidly giving changes in the ϵ values up to 30 % within a period of 2 h. These differences are probably due to a faster acid hydrolysis in this medium.

Prolonged treatment with 12 M hydrochloric acid at room temperature yielded within hours the green chloride salt of the *trans*-dichlorotetrakis(pyridine)cobalt(III) ion. The yield was rather poor (20 %), due to reduction to cobalt(II). In a test tube experiment the rate of hydrolysis of $[\text{Copoly}_4\text{CO}_3]^+$ was compared with that of $[\text{Cophen}_2\text{CO}_3]^+$ (phen = 1,10-phenanthroline) using 12 M hydrochloric acid. The latter compound changed its colour to that of the diaqua complex within a minute, while the pyridine complex had not reacted to any visible extent within 10 min.

In 12 M perchloric acid, the reaction also proceeds slowly, though much faster than in 12 M hydrochloric acid. At room temperature, the reaction is essentially complete within 10 min, yielding the *trans*-diaquatetrakis(pyridine)cobalt(III) ion.

The colours of neutral and dilute acid solutions are purely red, but on addition of large quantities of strong acids an instantaneous colour shift to red-violet is observed, independently of which acid is used.

The visible absorption spectra of the carbonatotetrakis(pyridine)cobalt(III) perchlorate in pure water, in aqueous 7.2 M lithium chloride solution, and in hydrochloric acid solutions (7.2, 9.4, and 12 M) are shown in Fig. 1. The spectrum of the neutral solutions remained constant for 3 h. The extinction values for the acid solutions varied with time, probably owing to the slow acid hydrolysis, and extrapolations back to the time of dissolution were necessary. The extrapolations were performed linearly, based upon absorption curves taken 2 and 7 min, respectively, after the time of dissolution. The corrections of the observed extinction values were only small (0–3 %) in 7.2 M and 9.4 M hydrochloric acid, but rather large (5–15 %) in 12 M hydrochloric acid.

Carbonatotetrakis(pyridine)cobalt(III) perchlorate is sparingly soluble in water and in 2 M perchloric acid but very soluble in 12 M perchloric acid. Thus it was possible to

dissolve the carbonato complex in 12 M perchloric acid at room temperature and reprecipitate the salt almost quantitatively by rapid dilution with five volumes of cold water.

As an attempt at obtaining a quantitative measure of the proton affinity, a determination of the solubilities in neutral and acid aqueous sodium perchlorate media was performed at $19 \pm 1^\circ\text{C}$. The concentrations were determined spectrophotometrically from the absorbancies at the maxima by comparison with the absorbancies of solutions of known concentrations. Saturated solutions in 4 M and in 8 M sodium perchlorate were obtained by treating a large excess of the perchlorate salt with the solvent until no increase in the absorbancy was observed. Saturation was achieved within 2 h. However, within 8 min a concentration of approximately 90 % of that in the saturated solution was observed. The preparation of the acid solutions was complicated by the acid hydrolysis. The solutions were therefore prepared and measured within 10 min, during which time the absorbancy of a solution at the first absorption band decreased less than 1 % to decrease much further as the acid hydrolysis took place. So errors due to the hydrolysis are estimated to be negligible. However, the solutions obtained in this manner were doubtless not saturated and the values given in Table 1 must therefore represent lower limits to the solubility in the acid media.

In order to further check that the higher concentrations found in the acid media were actually due to increased solubility, the following experiment was made. An almost saturated solution of the carbonato salt in 8 M NaClO_4 , 0.5 M HClO_4 was prepared as before. Then 38 ml of this solution was partly neutralized immediately after its preparation by addition of 3 ml of 5 M NaOH producing a solution with 7.8 M NaClO_4 , 0.1 M HClO_4 . Within 3 h red crystals separated. These were identified as $[\text{Copy}_4\text{CO}_3]\text{ClO}_4 \cdot \text{H}_2\text{O}$ by their Guinier powder diffraction pattern and by their infrared spectrum in the region $4000 - 250 \text{ cm}^{-1}$. The yield was 60 mg to be compared with the theoretical yield of $[\text{Copy}_4\text{CO}_3]\text{ClO}_4 \cdot \text{H}_2\text{O}$, 158 mg, calculated from the solubilities above.

The infrared spectrum of carbonatotetrakis(pyridine)cobalt(III) perchlorate was compared with that of trichlorotris(pyridine)cobalt(III) and showed clearly additional bands in the ν_1 [1680 (broad), 1640 (sharp) cm^{-1}] and ν_6 [1240 (shoulder) cm^{-1}] regions ^o of the bidentately coordinated carbonate ion.

3. *trans-Diaquatetrakis(pyridine)cobalt(III) perchlorate*, *trans*- $[\text{Copy}_4(\text{H}_2\text{O})_2](\text{ClO}_4)_3 \cdot 4\text{H}_2\text{O}$. Carbonatotetrakis(pyridine)cobalt(III) perchlorate (4 g, 7.24 mmol) was dissolved in 70 % perchloric acid (15 ml), and the violet solution allowed to stand at room temperature for 10 min under carbon dioxide evolution. The colour gradually changed to red-violet and a brownish precipitate, probably anhydrous *trans*-diaquatetrakis(pyridine)cobalt(III) perchlorate, formed. After cooling, ice-cold water (30 ml) was added. Thereby the precipitate dissolved and after a few seconds brown crystals of *trans*-diaquatetrakis(pyridine)cobalt(III) perchlorate with 4 mol of crystal water formed. After cooling for 10 min in ice, the precipitate was filtered, washed with ice-cold 4 M perchloric acid (5 ml) and sucked as dry as possible. Then the sample was dissolved in ice-cold 0.12 M perchloric acid (40 ml) and ice-cold 70 % perchloric acid (20 ml) was added to the filtered solution with stirring and cooling in ice. After some minutes the precipitate was filtered, washed with ice-cold 4 M perchloric acid (5 ml) and dried with ether.*

Drying in air yielded brown crystals (4.3 g) of pure *trans*-diaquatetrakis(pyridine)cobalt(III) perchlorate. (76 %). (Found: Co 7.50; N 7.16; C 30.26; Cl 14.38; H 3.7. Calc. for $[\text{Copy}_4(\text{H}_2\text{O})_2](\text{ClO}_4)_3 \cdot 4\text{H}_2\text{O}$: Co 7.54; N 7.17; C 30.72; Cl 13.60; H 4.1.) (ϵ , λ)_{max}: (43.9, 560); (51.0, 490). (ϵ , λ)_{min}: (43.3, 540); (25.8, 435). Medium: 1 M nitric acid.

Acid dissociation constant of the *trans*-diaquatetrakis(pyridine)cobalt(III) ion.

The first acid dissociation constant of the *trans*-diaquatetrakis(pyridine)cobalt(III) ion was determined at 25°C in 1 M NaNO_3 . The ion has an acidity comparable to that of phosphoric acid. Therefore the dissociation constant was calculated directly from pH

* Caution must be taken to avoid leaving the ether with the perchloric acid washings or the mother liquor.

measurements on solutions of the ion itself, or even better, of the ion itself in 0.01 M HNO₃.

As the complex is unstable in water and decomposes rather rapidly, the solutions were made up quickly so as to make the first measurement 30–45 sec after the dissolution. The measurements were continued over a period of 2 min and the pH data given in Table 3 are the results of a linear extrapolation back to the time of dissolution. The rate of change was in the order of 0.02 pH units per minute for the acid medium, 0.01 M HNO₃, 1 M NaNO₃, and 0.04 pH units per minute for the neutral medium, 1 M NaNO₃. So the rate of decomposition increases with increasing pH and the extrapolated pH-values are more accurate for the more acid solutions. The acid-dissociation constant was calculated¹⁰ by means of the equation:

$$-\log K_{s,1} = -\log [H^+] + \log \left(\frac{1 - \bar{\nu}}{\bar{\nu}} \right) + \log \left[1 + \frac{(2 - \bar{\nu})K_{s,2}}{(1 - \bar{\nu})[H^+]} \right] \quad (1)$$

where $\bar{\nu}$ equals the average number of protons produced by the diaqua ion and is given by $\bar{\nu} = ([H^+] - [OH^-] - C_{HNO_3})/C_{Co}$ where, for example, C_{Co} = stoichiometric concentration of the complex, and $-\log [H^+] = \text{pH}$ (measured). The last term of eqn. (1) was ignored in the calculations of $K_{s,1}$.

As seen from Table 3, the experimental uncertainty is rather large for the data obtained in 1 M NaNO₃ as compared with that in 0.01 M HNO₃, 1 M NaNO₃, although the averages for the two sets of experiments agree well.

Because of the fast decomposition already at $[H^+] = 0.01$ M, we were unable to determine, by this method, the second acid dissociation constant $K_{s,2}$ for the *trans*-diaqua ion. An order of magnitude estimate of $K_{s,2}$ could, however, be obtained from the measurements in the neutral medium using the equation¹⁰

$$K_{s,2} = \frac{\bar{\nu}[H^+]^2 + (\bar{\nu} - 1)[H^+]K_{s,1}}{(2 - \bar{\nu})K_{s,1}} \quad (2)$$

and the value (1.4×10^{-2} M) found for $K_{s,1}$. This estimate of $K_{s,2}$ (10^{-4} M) is as expected for such a diaqua ion and would, according to formula (1), give a correction smaller than 0.02 to $K_{s,1}$. This correction has not been made.

RESULTS AND DISCUSSION

Cobalt-carbonato bond breaking. In the following it is attempted to sum up some features which may be relevant for comparing the present system with other cobalt(III) carbonato systems. The discussion is complicated by the circumstance that it is not known whether the same reaction mechanism applies to the different carbonato systems. So it is probably not justified to discuss the relative rates of reaction on the basis of the following arguments which are essentially of thermodynamic character. Therefore the following discussion should be read with this reservation in mind.

Carbonatochlorotris(pyridine)cobalt(III) hydrolyses much faster with acid than does the carbonatotetrakis(pyridine)cobalt(III) ion. This is probably partly because its lower charge facilitates the attack of the hydrogen ion, but the below-mentioned reasons of sterical or electronic origins are likely to act in the same direction.

In order to try to understand¹¹ the different rates of hydrolysis of α - and β -[CotrienCO₃]⁺ (trien = triethylenetetramine = 1,4,7,10-tetraazadecane) it was natural to invoke the sterical differences between these two equally charged ions whose electronic situation should not be too different. On the other hand, by the comparison^{12,13} of the fast hydrolysis rates of [Coen₂CO₃]⁺

(en = ethylenediamine) and other analogous amine systems with the slow rates of $[\text{Cobipy}_2\text{CO}_3]^+$ (bipy = 2,2'-bipyridine) and $[\text{Cophen}_2\text{CO}_3]^+$ (phen = 1,10-phenanthroline), it was likely that the electronic properties of the N-ligating ligands were causing the main differentiating factor. Here the electron accepting capability of the heterocyclic aromatic ligands was proposed to increase the electron donation to the metal ion from the oxygen ligators of the carbonate ion and thereby strengthen the cobalt to oxygen bonds. This abolition of the charge accumulation on the cobalt by the π -acid character of the aromatic systems would seem likely to occur also with pyridine as the N-ligand, but in this case to a lower extent than with the larger aromatic ligands. On the other hand, all the aromatic ligands are probably poorer σ -donors than the amine systems with concomitant smaller charge accumulation on the cobalt, and this probably applies more to pyridine than to the bidentate heteroaromatics. Therefore, the fact that $[\text{Copy}_4\text{CO}_3]^+$ hydrolyses slowest of all the carbonato complexes mentioned, need not be caused by a steric inhibition of the hydrogen ion attack. However, from the X-ray structure analysis¹⁴ of $[\text{Copy}_4\text{CO}_3]\text{ClO}_4 \cdot \text{H}_2\text{O}$ it can be seen that the α -hydrogen atoms of some of the pyridine molecules do shield the ligating oxygen atoms.

The infrared spectra of carbonato-complexes have previously been compared and it has been advocated that the frequency ν_1 (1600–1650 cm^{-1}), which, according to normal coordinate analysis, essentially is associated with the carbon to oxygen double bond, increases as the cobalt to oxygen bond is strengthened.^{9,15} In the region of ν_1 the compound $[\text{Copy}_4\text{CO}_3]\text{ClO}_4 \cdot \text{H}_2\text{O}$ exhibits bands at 1680 (broad) and 1640 (sharp) to be compared with

$[\text{Co}(\text{NH}_3)_4\text{CO}_3]\text{Cl}$	1593; ⁹
$[\text{Co}(\text{ND}_3)_4\text{CO}_3]\text{Cl}$	1635, 1607; ⁹
$[\text{Coen}_2\text{CO}_3]\text{Br}$	1628, 1615; ⁹ 1575; ¹⁵ 1613, 1607; ¹²
$[\text{Coen}_2\text{CO}_3]\text{ClO}_4$	1643; ⁹
$[\text{Coen}_2\text{CO}_3]\text{Cl}$	1577; ¹⁵ 1613, 1590; ¹²
$[\text{Cobipy}_2\text{CO}_3]\text{Cl}$	1632; ¹³
$[\text{Cophen}_2\text{CO}_3]\text{Cl}$	1650, 1630. ¹²

It is seen that the pyridine complex has the highest ν_1 frequency, which should mean the highest cobalt to oxygen bond order, in agreement with its higher stability toward hydrolysis.

Protonation of the carbonato group. A reasonably concentrated solution of $[\text{Copy}_4\text{CO}_3]\text{ClO}_4$ in 12 M perchloric acid reprecipitates the complex perchlorate on addition of water. This would seem to indicate that a protonation had taken place. On the other hand, we have found that $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$ dissolves in hydrochloric acid, saturated with HCl at 0°C, and reprecipitates on addition of water. Further, Pfeiffer¹⁶ reports that $[\text{Cry}_3\text{Cl}_3]$, which does not dissolve much in concentrated hydrochloric acid, dissolves very well in concentrated nitric acid and reprecipitates on addition of water. We can confirm Pfeiffer's report and add that concentrated perchloric acid does not dissolve $[\text{Cry}_3\text{Cl}_3]$ equally well, and it seems unlikely that a well defined protonation takes place, either with $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$ or with $[\text{Cry}_3\text{Cl}_3]$.

In the following, evidence will be presented that the carbonato group of

$[\text{Copy}_4\text{CO}_3]^+$ is protonated in at least two steps. The first protonation is demonstrated by solubility measurements, and the further protonation by spectrophotometric measurements.

A quantitative study of the protonation was made by the solubility measurements given in Table 1. The results show unambiguously that a protonation does take place and the variation of solubility with acid concentration shows further that one proton is taken up by the carbonato ion – in this $[\text{H}^+]$ -region and this medium – and not two at a time.

Table 1. Solubilities of $[\text{Copy}_4\text{CO}_3]\text{ClO}_4 \cdot \text{H}_2\text{O}$ in different media (19°C). For the acid media the data are lower limits to the solubilities.

Medium	Concentration $\times 10^8$
8 M NaClO_4	5.1 M
8 M NaClO_4 , 0.1 M HClO_4	6.1 M
8 M NaClO_4 , 0.5 M HClO_4	14 M
7.5 M NaClO_4 , 0.5 M HClO_4	12 M
4 M NaClO_4	3.1 M
4 M NaClO_4 , 0.5 M HClO_4	5.1 M

The acid dissociation constant K for $[\text{Copy}_4\text{CO}_3\text{H}]^{2+}$, applicable for the medium 7.5–8 M sodium perchlorate, may be estimated as $K=0.3$ M from the solubilities. For the medium 4 M sodium perchlorate K is estimated as $K=0.7$ M, or twice the above value. This increase of the basic character of $[\text{Copy}_4\text{CO}_3]^+$ ion with increasing salt concentration is also reflected in the rate of acid hydrolysis which increases considerably on going from 1 M HCl to 1 M HCl , 6 M LiCl .

It seems to be a general feature of normal salts that their “salting-in” effect on the protonated species (which always has a positive charge which is higher than that of the base by one unit) is the dominating factor to determine the decrease of the acidity constant with increasing salt concentration. This variation has been found before for some cationic chromium(III) complexes,¹⁷ and it is also known for some neutral amines, e.g. 4-nitroaniline,^{18a} although the salting-out effect on the base may be of importance here. It is noteworthy that with 4-nitroaniline the variation is the opposite when the salt is tetraethylammonium chloride, probably because this organic cation interacts more with the neutral amine than with its cationic corresponding acid.

The protonation of $[\text{Copy}_4\text{CO}_3]^+$ was further studied by comparing the visible spectra in different media (Table 2, Fig. 1). There are two noteworthy features.

Solutions of $[\text{Copy}_4\text{CO}_3]\text{ClO}_4$ in salt media are more violet than are water solutions of the same concentration. This is associated with a red shift of the first absorption maximum of 4 nm and an increase in the molar absorptivity of 1–2 %. This would normally be called a medium effect meaning that we know of no specific chemical interaction that can be made responsible for it. It is nearly independent of the cation, provided this is not a proton. If it is a proton the red-shift of the first absorption band is larger and gradually in-

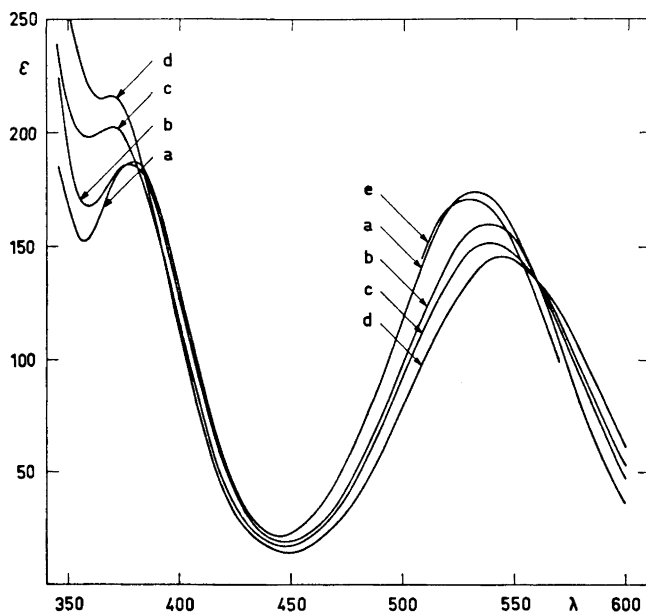


Fig. 1. Visible absorption spectra of $[\text{Copy}_4\text{CO}_3]\text{ClO}_4 \cdot \text{H}_2\text{O}$ at room temperature. 7.2 M LiCl (a), 7.2 M HCl (b), 9.6 M HCl (c), 12 M HCl (d) and water (e).

Table 2. Spectral data for $[\text{Copy}_4\text{CO}_3]\text{ClO}_4$ in different media.

Medium	$(\epsilon, \lambda_{\text{max}})$	$(\epsilon, \lambda_{\text{max}})$
H_2O	(172,530)	(190,379)
6 M LiCl	(174,532)	(187,379)
7.2 M LiCl	(175,532)	(187,378)
12 M LiCl	(174,534)	(188,376)
6 M CaCl_2	(174,534)	(192,376)
4.5 M MgCl_2	(177,534)	(191,376)
0.5 M HCl, 6 M LiCl	(172,532)	(186,378)
1 M HCl, 6 M LiCl	(171,533)	(185,377)
7.2 M HCl	(160,538)	(187,377)
12 M HCl	(146,544)	(215,370) ^a
8 M NaClO_4	(173,532)	(183,379)
0.5 M HClO_4 , 8 M NaClO_4	(167,533)	(183,378)
4 M HClO_4	(164,535)	(187,379)
7.2 M HClO_4	(145,543)	(213,370) ^a

^a The maximum not developed, appears as a shoulder.

creases with the acid concentration to 14 nm and there is a concomitant decrease in the molar absorptivity up to 15 %. This special behaviour of the proton is attributed to protonation of the carbonato complex.

However, the visible absorption spectrum in 0.5 M HClO₄, 8 M NaClO₄ is almost identical with the spectrum in 8 M NaClO₄. As approximately 60 % of the complex is protonated in the acid solution, this means that the absorption spectrum of the carbonato complex is almost unaffected by this first protonation. This observation is in agreement with the fact that the visible absorption spectra in 6 M LiCl and 0.5 M HCl, 6 M LiCl also are nearly identical.

The knowledge that [Copy₄CO₃]⁺ and [Copy₄CO₃H]²⁺ have similar spectra makes it necessary to attribute the changes of the spectra in strongly acid solutions (Table 2, Fig. 1) to protonation beyond the first proton but it cannot be inferred from the results whether one or more further protons are taken up.

It would be chemically interesting to know where the protons are bound in the carbonato ion. There are three places that one may discuss, the carbonyl oxygen atom and the two ligating oxygen atoms.

The fact that the spectra of [Copy₄CO₃]⁺ and [Copy₄CO₃H]²⁺ are almost identical would suggest that the first proton is located upon the carbonyl oxygen. It should, however, be noted that the [H⁺]-independent equilibria between species with differently located protons might invalidate this suggestion to a small extent.

The fact that the second protonation is associated with a colour shift is in agreement with the assumption that this protonation takes place on the ligating oxygen atoms.

Finally, there are two facts that we would like to mention. Firstly, the spectrum of [Copy₄CO₃]ClO₄ in 7.2 M perchloric acid resembles that in 12 M hydrochloric acid (Table 2). Secondly, the rate of acid hydrolysis in 12 M perchloric acid as compared with 12 M hydrochloric acid is pronouncedly increased. These results agree qualitatively with the circumstance that perchloric acid in non-aqueous media is a stronger acid than hydrochloric acid and that the same applies to aqueous media for very high acid concentrations.^{18b}

trans-Diaquatetrakis(pyridine)cobalt(III) perchlorate. The reaction of the carbonatotetrakis(pyridine)cobalt(III) ion with perchloric acid is unusual not only because it is very slow but also because of the fact that the reaction* leads to the *trans*-diaquatetrakis(pyridine)cobalt(III) ion. In contrast to this, the acid hydrolysis of the corresponding carbonato complexes with ammonia and ethylenediamine⁵ yields the *cis* isomers.

The assignment of the *trans* structure of the diaquatetrakis(pyridine)-cobalt(III) ion is unambiguous, based on the visible absorption spectrum which exhibits a tetragonal splitting of the first spin-allowed absorption band ¹A_{1g}(O_h) → ¹T_{1g}(O_h) into clearly separated components ¹A_{1g}(D_{4h}) → ¹E_g(D_{4h}) [17 860 cm⁻¹] and ¹A_{1g}(D_{4h}) → ¹A_{2g}(D_{4h}) [20 410 cm⁻¹], analogously to the corresponding ethylenediamine complex.¹⁰

The first acid dissociation constant (10^{-1.37} M in 1 M NaNO₃) of the *trans*-diaquatetrakis(pyridine)cobalt(III) ion is pronouncedly higher than that

* It may be noted that in the reaction with 12 M hydrochloric acid the first isolable product is the chloride of the *trans*-dichlorotetrakis(pyridine)cobalt(III) ion.

Table 3. The first acid-dissociation constant of the *trans*-diaquatetrakis(pyridine)cobalt(III) ion in 1 M NaNO₃ at 25°C.

0.01000 M HNO ₃ , 1 M NaNO ₃					
No.	C _{co}	-log[H ⁺]	[H ⁺]	$\bar{\nu}$	pK _{s,1}
1	0.01494	1.694	0.02023	0.6847	1.358
2	0.02020	1.639	0.02296	0.6416	1.386
3	0.02232	1.616	0.02421	0.6366	1.373
Average of pK _{s,1}					1.37

1 M NaNO ₃					
No.	C _{co}	-log [H ⁺]	[H ⁺]	$\bar{\nu}$	pK _{s,1}
1	0.01703	1.876	0.01331	0.7816	1.322
2	0.02095	1.831	0.01476	0.7045	1.453
3	0.02698	1.732	0.01854	0.6872	1.390
Average of pK _{s,1}					1.39

(10^{-4.15} M in 1 M NaNO₃)¹⁰ of the corresponding ethylenediamine complex. These results mean that the hydroxo complexes are more stable relative to the corresponding aqua complexes when the remaining ligands are pyridine molecules than when they are ethylenediamine molecules. This can be rationalized along similar lines to those mentioned on p. 3318.

Acknowledgement. We are grateful to Jannik Bjerrum for valuable comments which led to the discussion of the second protonation.

REFERENCES

1. Werner, A. *Ber.* **39** (1906) 1538.
2. Cheng, P.-T., Loescher, B. R. and Nyburg, S. C. *Inorg. Chem.* **10** (1971) 1275.
3. Raichart, D. W. and Taube, H. *Inorg. Chem.* **11** (1972) 999.
4. Delépine, M. and Lareze, F. *Compt. Rend.* (a) **256** (1963) 3912; (b) **257** (1963) 3772.
5. Krishnamurty, K. V., Harris, G. M. and Sastri, V. S. *Chem. Revs.* **70** (1970) 171.
6. Piriz Mac-Coll, C. R. *Coord. Chem. Revs.* **4** (1969) 147.
7. Jørgensen, C. K. *Inorganic Complexes*, Academic, London 1963, p. 81.
8. Hofmann, K. A. *Ber.* **38** (1905) 1999.
9. Fujita, J., Martell, A. E. and Nakamoto, K. *J. Chem. Phys.* **36** (1962) 339.
10. Bjerrum, J. and Rasmussen, S. E. *Acta Chem. Scand.* **6** (1952) 1265.
11. Dasgupta, T. P. and Harris, G. M. *J. Am. Chem. Soc.* **93** (1971) 91.
12. Farago, M. E., Keefe, I. M. and Mason, C. F. V. *J. Chem. Soc. A* **1970** 3194.
13. Francis, D. J. and Jordan, R. B. *Inorg. Chem.* **11** (1972) 461.
14. Kaas, K. and Sørensen, A. M. *Acta Cryst.* **B 29** (1973) 113.
15. Gatehouse, B. M., Livingstone, S. E. and Nyholm, R. S. *J. Chem. Soc.* **1958** 3137.
16. Pfeiffer, P. *Z. Anorg. Chem.* **55** (1907) 97.
17. Josephsen, J. and Schäffer, C. E. *Acta Chem. Scand.* **24** (1970) 2929.
18. Rochester, C. H. *Acidity Functions*, Academic, London 1970, (a) p. 101, (b) p. 39 and p. 43.

Received June 6, 1973.

Acta Chem. Scand. **27** (1973) No. 9