Thermochimica Acta, 8 (1974) 291–301
© Elsevier Scientific Publishing Company, Amsterdam – Printed in Belgium

SOME THERMODYNAMIC PROPERTIES OF CARBOXYLATO-PENTAMMINE COBALT(III) IONS

R. J. LEMIRE AND M. W. LISTER
Lash Miller Chemical Laboratories, University of Toronto, 80 St. George Street, Toronto (Canada)

(Received 16 July 1973)

ABSTRACT

Measurements are reported on the thermodynamic properties for the acid ionisation of various carboxylato-pentammine cobalt(III) ions, where the organic ligand is a dicarboxylate ion $^{-}$OCORCOOH. It is shown that the results can be correlated with the ionisation of the free acids, on the basis of a simple electrostatic model. Results are also reported on the enthalpies of hydrolysis of the same ions, obtained indirectly from the enthalpies of reaction with sodium sulphide. The results for the complexes of the dicarboxylic acids which were studied (maleato, phthalato, fumarato, succinato and malonato) are not very different, while the acetato complex is somewhat more unstable. There is some indication that the complexes which hydrolyse faster are also thermodynamically less stable.

INTRODUCTION

Ions of the general formula $Co(NH_3)_5X^{n+}$, where X is anionic, have been the subject of considerable investigation, particularly as regards the replacement of the X group by water[1], and their reduction by ions such as Cr^{2+} [2–4]. Amongst these ions, those of formula $Co(NH_3)_5OCORCOO^+$, or the protonated $Co(NH_3)_5OCOR\cdot COOH^{2+}$, where R is an organic group, form a series of similar species, which offer opportunities for comparisons of their rates of reaction[5] with the object of elucidating their reaction mechanisms. Of related interest are various thermodynamic properties of these compounds, particularly the strength of the bond joining the cobalt to the carboxylate group, and their acid–base properties. These latter properties should, of course, be compared with those of the free carboxylic acids, or their ions. The present paper is concerned with these thermodynamic aspects of these compounds. The central group, R, was chosen to give chains of different length, and also to allow the possibility of conjugation along the chain.

A difficulty arises in attempts to measure the strength of bonding of the carboxylate group in that reactions such as

$$Co(NH_3)_5OCORCOO^+ + OH^- \rightarrow Co(NH_3)_5OH^{2+} + R(CO_2)_2^{2-}$$

are fairly slow[5] at room temperature, and may be complicated by side reactions. Thus, while measurements of their enthalpy would probably offer the best basis for comparison, they are not very convenient for calorimetry. Accordingly the reaction of these compounds with aqueous sodium sulphide was used, a method originating with Lamb and Simmons[6], and more recently used fairly extensively by Yatsimirsky and Pankova[7,8]. Some comments on the reliability of the method will be made later. Although the main object of the present work was a comparison of these cobalt complexes among themselves, the measurements permit their enthalpies of formation to be calculated.

EXPERIMENTAL

Chemicals

Pentammineaquo cobalt(III) perchlorate was prepared from carbonatopentammine cobalt(III) perchlorate, which was synthesised by the method of Basolo and Murmann[9]. The carbonate complex was dissolved in a minimum amount of water at 80°C, and to this was added a large excess of 70% perchloric acid. On cooling, $[Co(NH_3)_5H_2O](ClO_4)_3$ crystallised, and was filtered off and washed with absolute ethanol, and then with diethyl ether. Gould and Taube[10] report that the material so prepared may be contaminated with the tetraammine complex, but it was found that this was avoided if the initial precipitate in the preparation of the carbonato complex was immediately redissolved. The pentammineaquo cobalt(III) perchlorate was purified by twice dissolving it in water, and re-precipitating it with 70% perchloric acid, followed by a final recrystallisation from 0.05 M perchloric acid. On analysis it gave: hydrogen 3.73% (calculated 3.72%); chlorine 23.12% (calculated 23.10%).

Acetatopentammine cobalt(III) perchlorate was prepared by the method of Jackman, Scott and Portman[11], followed by recrystallisation from water and from dilute perchloric acid. Analysis gave: carbon 5.86% (calculated 5.97%); hydrogen 4.54% (calculated 4.51%); chlorine 17.71% (calculated 17.64%).

Acidopentammine cobalt(III) perchlorates. Other compounds with dicarboxylato groups as the anion attached to cobalt were prepared either as described by Jackman et al.[11], or as follows. About 10 gram of the pentammineaquo cobalt(III) perchlorate was suspended in 125 ml of water. A ten-fold excess of the appropriate dicarboxylic acid (reagent grade) was added, as was 1 gram of sodium hydroxide. The mixture was kept at 70–80°C with stirring for three hours, then cooled and filtered. The solution was passed through a column of cation exchange resin in hydrogen form, either Rexyn 102 or Dowex 50W–X8. The column was washed with water to remove free dicarboxylic acid, and then eluted with 3 M perchloric acid. The eluted solution was cooled in ice, and a few ml of 70% perchloric acid was added to precipitate the acidopentammine cobalt(III) perchlorate, which was filtered off and washed with ethanol.

Compounds prepared by either method were recrystallised from 0.1 M perchloric acid, washed with ethanol followed by diethyl ether, and finally dried under vacuum. It may be added that preparation of the phthalato and succinato complexes by the method of Jackman, Scott and Portman[11] does not seem to have been reported previously, although the extension is obvious.

Analysis of each product is given in Table 1. The formula was confirmed by dissolving a weighed sample in water, and titrating with standard NaOH.

TABLE 1

Compound	*% C*	*% H*	*% Cl*	*% N*
Malonato $[Co(NH_3)_5OCOCH_2CO_2H](ClO_4)_2$	8.27 (calc 8.08)	4.14 (calc 4.07)	15.94 (calc 15.90)	
Fumarato $[Co(NH_3)_5OCOCH{:}CHCO_2H](ClO_4)_2$	10.26 (calc 10.94)	4.4 (calc 4.0)	15.59 (calc 15.40)	
Maleato same formula	10.29	3.6	15.63	
Phthalato $[Co(NH_3)_5OCOC_6H_4CO_2H](ClO_4)_2$	18.61 (calc 18.91)	3.97 (calc 3.97)	14.13 (calc 13.95)	
Succinato (crystallised as the hemi-perchloric acid adduct) $[CoCNH_3)_5CCOCH_2CH_2CO_2H]$-$(ClO_4)_2 \cdot \frac{1}{2}HClO_4$	9.54 (calc 9.42)	4.1 (calc 4.05)	17.60 (calc 17.47)	13.89 (calc 13.73)

Sodium sulphide. A reagent grade sample was crystallised as $Na_2S \cdot 9H_2O$, which was dehydrated over sulphuric acid. Solutions were prepared immediately before use.

Sodium hydroxide. A carbonate free 50% solution (Fisher Certified Reagent) was diluted with freshly boiled distilled water. The solution was standardised against potassium hydrogen phthalate.

Other substances used in the preparations or measurements were all reagent grade chemicals.

Apparatus

pH measurements. The ionisation constants of the acids were measured by following the pH of a solution of the acid during titration with sodium hydroxide. The pH was measured on a Beckmann Research Model pH-meter using a glass electrode and calomel reference electrode. A known weight of the acid in a known volume of solution was titrated with standardised sodium hydroxide, with stirring, in a closed beaker immersed in a thermostat at 25.00 ±0.01 °C. The pH readings were standardised by 0.05 M potassium hydrogen phthalate, before and after each run. All runs were done in duplicate.

pK_a values were calculated from each point in a run, usually about ten in all. The root mean square deviations from the means in any run, and the differences between the averages for duplicate runs, were both about 0.01. Hence each final pK_a value is probably ±0.01.

Calorimetry. Calorimetric measurements were made on the reactions of the carboxylatopentammine cobalt(III) ions both with sodium hydroxide, and with sodium sulphide. In the former case, the cobalt compound was always in excess, so that the reaction was simply that of the -COOH group with OH^-. Excess hydroxide was avoided, as it caused aquation of the complex.

The calorimeter was similar to one described earlier[12]. The temperature was measured by a 2000 Ω thermistor (Fenwal GB32P28), with a temperature coefficient of -3.2% per degree at 25°C. This was contained in a wheatstone bridge circuit with 2000 Ω resistors in each arm, and a 1.35 V mercury cell. Any off-balance voltage was detected by a Model 885A DC differential voltmeter (John Fluke Manufacturing Co. Inc.). The voltmeter could be read reliably to 1 microvolt, which corresponded to 2×10^{-4} degrees. The calorimeter, as usual, was calibrated electrically. The heating time was between 100 and 200 sec., measured to 0.05 sec. The heating current was measured by the voltage drop across a precision 1 Ω resistor, kept at 25.0°C, and calibrated to 1 part in 10^5. This, and the heating voltage, were measured on a Leeds and Northrup precision potentiometer (Model 7552) in conjunction with a Leeds and Northrup galvanometer (Model 2430); these gave a precision of better than 5×10^{-5} V in these measurements. The actual heating voltage varied according to the experiment, but was typically about 10 V; the heater resistance was 200 Ω.

In the neutralisation reactions about 8×10^{-4} mole of NaOH (accurately measured) reacted with excess acid. The heat capacity of the calorimeter plus solution was about 1000 J/degree, and the temperature rise about 0.06°. In the reactions with sodium sulphide, about 10^{-3} mole of the cobalt compound was mixed with a large excess of 0.25 M Na_2S, the resulting temperature rise being about 0.1°. Blank runs were, of course, performed with both types of measurement.

RESULTS

pK_a values

The results given below are the thermodynamic ionisation constants, K_a°. If XH^{2+} is the complex cobalt ion, K_a° is defined as $K_a^\circ = a_{H^+}a_{X^+}/a_{XH^{2+}}$. The pH meter reading gave the value of a_{H^+}. For the other species, it was assumed that the activity coefficient was given by the extended Debye–Hückel equation:

$$-\log f_\pm(z_1, z_2) = A|z_1 z_2| \left\{ \frac{\sqrt{I}}{1+b\sqrt{I}} - cI \right\}$$

where $f_\pm(z_1, z_2)$ is the mean activity coefficient for a compound with charges of z_1 and z_2 on the ions. I is the ionic strength, and A is the Debye–Hückel constant. A mean value of $b = 1.5\ M^{-1/2}$ was used for all the complex cobalt ions; c was taken to be $0.2\ M^{-1}$, as suggested by Davies[13]. The activities of the cobaltic species could be determined from their concentrations, and the calculated activity coefficients. The concentrations were obtained from the usual mass balance or charge balance equations. As it was necessary to assign a value to the activity coefficient of the hydrogen ion, and this in turn depended on the ionic strength, the value used for the ionic strength was adjusted till it was consistent with both the mass balance and activity coefficient equations.

TABLE 2

pK_a VALUE OF ACIDOPENTAMMINE COBALT(III) IONS AT 25°C, $I=0$

Acidic ligand	*pK_a*	*RMS Deviation*	*Mean value*
Hydrogen–maleato	2.466	0.009	2.462
	2.457	0.017	
Hydrogen–phthalato	2.309	0.012	2.316
	2.323	0.013	
Hydrogen–fumarato	3.017	0.022	3.020
	3.022	0.025	
Hydrogen–succinato	3.815	0.010	3.817
	3.819	0.009	
Hydrogen–malonato	3.121	0.010	3.116
	3.110	0.010	
Aquo	5.582	0.008	5.576
	5.570	0.011	

The mean values of pK_a are for 9 to 12 points covering the range of 0 to 90% neutralisation. Table 2 gives the results with the root mean square deviation for each run. The final value is the mean of duplicate runs. The results in Table 2 can be compared with literature values, in general for somewhat different conditions: hydrogen–maleato, 2.6 ($I=1.0$, 25°C)[3]; hydrogen–fumarato, 3.2 ($I=1.0$, 25°C)[3]; hydrogen–succinato, 3.9 ($I=1.0$, 25°C)[15]; hydrogen–malonato, 3.4 ($I=0.1$, 25°C)[16]; aquo, 5.69 ($I=0$, 15°C) [17]and 6.18 ($I=0.1$, 20°C)[18]. There is no marked discrepancy with earlier values, if we allow for the somewhat different conditions.

Enthalpy of ionisation

The enthalpy of ionisation of any acidopentammine cobalt(III) complex was obtained from the difference between its enthalpy of reaction with a given amount of sodium hydroxide, and that of perchloric acid with the same amount. This difference was divided by the number of moles of acid ionising, which could be calculated from the pK_a values obtained earlier. The results are given in Table 3. Each result is the mean of three determinations, and the average deviation of the results from the mean varied from 0.1 J (for perchloric acid) to 0.25 J. The acid was always in excess: 9.290×10^{-4} moles acid to 7.955×10^{-4} moles of NaOH in a total volume of 243.0 ml. From the number of determinations and spread of results, the enthalpy of ionisation is probably ±0.4 kJ mole^{-1}, which is a fairly large percentage error arising from the fact that the final result is a small difference of two much larger quantities.

These data allow $\Delta G°$ and $\Delta S°$ also to be calculated for these reactions, and the results are in Table 4. The values of $\Delta H°$ in Table 3 are for slightly different ionic

TABLE 3

ENTHALPIES OF REACTION OF ACIDOPENTAMMINE COBALT(III) IONS WITH SODIUM HYDROXIDE AT 25 °C

Acidic ligand	*Enthalpy of reaction*[a] *(Joules)*	*Moles of acid ionised* × 10^4	*Enthalpy of ionisation* *(kJ mole*$^{-1}$*)*
Hydrogen–maleato	−46.65	3.325	-5.1_5
Hydrogen–phthalato	−46.07	2.897	−3.9
Hydrogen–fumarato	−44.48	4.889	0.9_5
Hydrogen–succinato	−44.18	6.506	1.1_5
Hydrogen–malonato	−45.52	5.126	-1.1_5
Aquo	−12.59	7.745	41.7_5
Perchloric acid	−44.94	7.955	—

[a] This includes the heating of opening the NaOH container.

TABLE 4

THERMODYNAMIC QUANTITIES FOR THE IONISATION OF ACIDOPENTAMMINE COBALT(III) IONS AT 25 °C

Acidic ligand	ΔG° *(kJ mole*$^{-1}$*)*	ΔH° *(kJ mole*$^{-1}$*)*	ΔS° *(J degree-mole*$^{-1}$*)*
Hydrogen–maleato	14.0_5	-5.1_5	$-64._5$
Hydrogen–phthalato	13.2	−3.9	$-57._5$
Hydrogen–fumarato	17.2	0.9_5	−55
Hydrogen–succinato	21.8	1.1_5	−69
Hydrogen–malonato	17.8	-1.1_5	$-63._5$
Aquo	31.8	41.7_5	33

TABLE 5

ENTHALPIES OF REACTION OF ACIDOPENTAMMINE COBALT(III) IONS WITH SODIUM SULPHIDE, AND DERIVED ENTHALPIES

Acidic ligand	ΔH° *(Na_2S)* *(kJ)*	ΔH° *(reaction 1)* *(kJ)*	ΔH° *(reaction 2)* *(kJ)*
Acetato	−57.7	−7.9	−22.2
Hydrogen–maleato	−107.5	4.2	−7.9
Hydrogen–phthalato	−105.0	1.7	−10.9
Hydrogen–fumarato	−108.4	2.1	−15.9
Hydrogen–succinato	−106.7	0.8	−14.2
Hydrogen–malonato	−105.9	2.1	−14.6
Aquo	−49.8	—	—

strengths, depending on the pK_a of the acid. In a typical case (the fumarato complex), the initial ionic strength was 0.0102, and after addition of sodium hydroxide it was 0.0081; in every case the ionic strength was close to 0.01. In the calculations of ΔS°, it was assumed that ΔH° was the same at zero ionic strength, and could therefore be combined with the ΔG° values.

The enthalpies of reaction with excess sodium sulphide are given in Table 5. These ΔH° values are per mole of cobalt complex, that is for the reactions in aqueous solution (0.08 M complex with 0.25 M sodium sulphide).

$$\mathrm{Co(NH_3)_5OCORCOOH(ClO_4)_2 + \tfrac{5}{2}Na_2S \rightarrow \tfrac{1}{2}Co_2S_3 + 5NH_3 + Na_2R(CO_2)_2 + NaHS + 2NaClO_4.}$$

Table 5 also contains ΔH° calculated for

$$\mathrm{Co(NH_3)_5OCORCOOH^{2+} + H_2O \rightarrow Co(NH_3)_5H_2O^{3+} + R(CO_2H)CO_2^-} \quad (1)$$

and the related ΔH° for

$$\mathrm{Co(NH_3)_5OCORCO_2^+ + OH^- \rightarrow Co(NH_3)_5OH^{2+} + R(CO_2)_2^{2-}} \quad (2)$$

To obtain these we need the enthalpy of reaction of pentammineaquo cobalt(III) perchlorat with excess sodium sulphide, which was measured and recorded in Table 5. We also need enthalpy data on the ionisation of the cobalt compounds (given earlier), and of the free carboxylic acids given by Christensen, Izatt and Hansen[19]. In addition ΔH° for

$$\mathrm{Na_2S + HClO_4 \rightarrow NaHS + NaClO_4}$$

is needed; this was measured at the concentrations of the other experiments and gave $\Delta H^\circ = -57.0$ kJ. It was checked that ammonia in the concentrations produced in the reactions had no effect on this.

The value for the aquo compound may be compared with Yatsimirsky and Pankova's[7] value of −49.4 kJ. These results are less accurate than those of the ionisation reactions, in part because the precipitated cobalt(III) sulphide, while it seems to be reproducible, is probably not as well defined as species in solution. Each result in Table 5 is the mean of three measurements (four for the aquo compound), and the average deviation from the mean was 0.6 to 0.7 kJ. In addition, the extent of ionisation in the initial solution has to be calculated, which adds a small extra uncertainty. Hence it can only be claimed that the results are ± 1.0 kJ.

It is possible, from the data in Table 5 and in the literature, to calculate the conventional enthalpies of formation of these cobaltic species. This calculation uses the enthalpies of combustion of the carboxylic acids, their enthalpies of solution (obtained in large part from solubility data), and the enthalpy of formation of $\mathrm{Co(NH_3)_5H_2O^{3+}(aq)}$. Unfortunately the last quantity is very variously quoted. Krestov and Yatsimirsky[20] give −806.7 kJ, and U.S. National Bureau of Standards[21] give −760.2 kJ. Using the latter value, the results are: acetate −956; hydrogen-fumarato, −1257; hydrogen-maleato, −1248; hydrogen-phthalato, −1209; hydrogen-succinato, −1381; and hydrogen-malonato, −1355 kJ. Since many pieces of data go into each value, no great accuracy can be claimed.

DISCUSSION

Various authors have suggested relations that might be expected to hold between the thermodynamic quantities in proton ionisations[22]. In particular, Christensen, Izatt and Hansen[19] consider the relations to be expected between these quantities for the two stages of ionisation for a dicarboxylic acid (see also ref. 21). The free energy of ionisation is divided into a "non-electrostatic" part, presumably associated with the breaking of a covalent bond and the formation of a new one by the proton with the solvent, and an electrostatic part arising from the separation of the two charged ions. In comparing the two stages of ionisation the non-electrostatic part may be supposed to be the same. Hence

$$\Delta G_2^\circ - \Delta G_1^\circ = \Delta G(\text{electrostatic}) + RT \ln \sigma$$

where ΔG_1, ΔG_2 are the free energy changes for the two stages, and $RT \ln \sigma$ is a statistical factor arising simply from the number of sites for ionisation or recombination. For a dicarboxylic acid, $\sigma = 4$. ΔG(electrostatic) is taken to be $-z_1 z_2 e^2/\varepsilon r$; where z_1 and z_2 are the charges on the ions, ε is the appropriate dielectric constant, and r is a somewhat ill-defined distance between the site of the negative charge already present in AH^- (where H_2A is the acid) and the initial position of the second ionising proton. On these assumptions, we should then expect that

$$\Delta G(\text{electrostatic}) = \left(\frac{\partial \ln \varepsilon}{\partial T}\right)_p^{-1} \Delta S(\text{electrostatic}).$$

If ε is the dielectric constant of the solvent, then for water at 25 °C

$$\Delta G(\text{electrostatic}) = -218\ \Delta S(\text{electrostatic})$$

This relation should hold equally well for the difference of ΔG° for the ionisation of the free acid HO_2CRCO_2H, and the complex ion $Co(NH_3)_5O_2CRCO_2H^{2+}$. Table 6 gives the results. In this table, ΔG(elec., acid) is the electrostatic free energy term defined above, using $\Delta G_2^\circ - \Delta G_1^\circ$ for the two stages of ionisation of the acids. ΔG(elec., complex) is similarly the electrostatic free energy term using $\Delta G^\circ_{\text{complex}} - \Delta G_1^\circ$

TABLE 6

ELECTROSTATIC CONTRIBUTIONS TO THERMODYNAMIC QUANTITIES

Acid	*ΔG(elec., acid) (kJ)*	*ΔS(elec., acid) (J deg^{-1})*	*ΔG(elec., complex) (kJ)*	*ΔS(elec., complex) (J deg^{-1})*
Maleic	21.8	−80	1.4	−23
Phthalic	10.6_5	−30.5	-5.3_5	15
Fumaric	5.1_5	−28	-2.1_5	9
Succinic	4.7	−26	-3.9_5	6
Malonic	12.9_5	−60.5	−0.1	−7.5

and a statistical factor $\sigma = 2$. ΔS(electrostatic) terms are similarly derived from

$$\Delta S_2^\circ - \Delta S_1^\circ = \Delta S(\text{electrostatic}) - R \ln \sigma$$

Data are from the present work or Ref. 19. The least mean squares line through a plot of ΔG(elec.) against ΔS(elec.) in Fig. 1, using all data in Table 6, gives

$$\Delta G(\text{elec.}) = -1.5 - 261\ \Delta S(\text{elec.}).$$

As can be seen the points from the cobalt complexes follow roughly the same line as do the points from the acids alone. The slope of the line is roughly 20% too high, as calculated for water at 25°C; but there is always the uncertainty that part of the material between the charges is the acid and not water, and also (especially for the cobalt complexes) that the dielectric constant of the water may be considerably reduced by the large field of the ions.

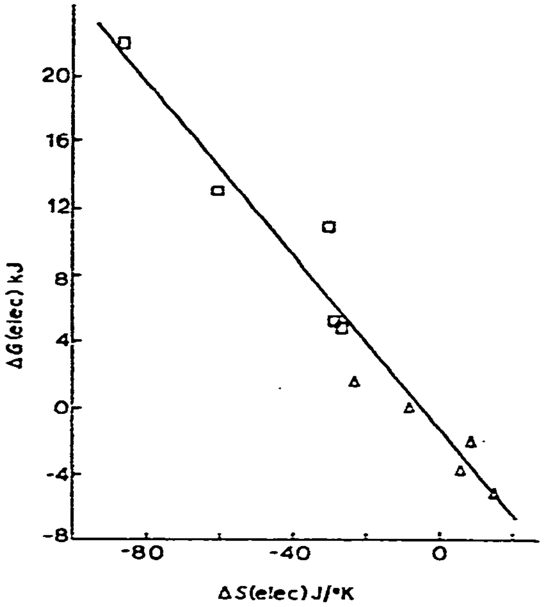

Fig. 1. Electrostatic contributions to free energy and entropy of dicarboxylic acids and their cobalt pentammine complexes. □, dicarboxylic acids; △, cobalt complexes.

ΔG(elec.) is always more negative for the cobalt complexes, as is to be expected, since the positive charge on the cobalt repels the proton. For the free acids there is some correlation between ΔG(elec.) and the distance between the carboxylic acid groups; at least to the extent that the cis geometry in maleic acid gives a bigger term than the trans geometry in fumaric acid, or the shorter chain in malonic gives a bigger term than the longer chain in succinic acid. This correlation does not hold for the cobalt complexes. However to a slight extent a more positive ΔG(elec., acid) correlates with a more positive ΔG(elec., complex), and the same is true of ΔS. It is hard to suggest a reason for this.

It may be noted that all these acids, except fumaric acid, can possibly be involved in internal hydrogen bonding. Westheimer and Benfey[23] have deduced that the effect of this is usually small. From our results, there is no indication that fumaric acid is out of line, either in the cobalt complex or the free acid; so probably internal hydrogen bonding is unimportant in the aqueous solutions of these cobalt complex ions.

If we now look at the enthalpies of the aquation of these complex ions (Table 5), perhaps the most remarkable feature is the considerable similarity of ΔH° for these reactions, with the exception of the acetato complex. This suggests that the more remote part of the dicarboxylic acid really does little to affect the strength of the bond to cobalt, and that effects such as possible delocalisation of the charge by means of conjugated double bonds are relatively unimportant. It is true that the acids with saturated chains are among the low ΔH° (reaction 1) values, but the effect is minimal. The slightly greater stability of the maleato compound, as compared with the fumarato complex, may possibly reflect hydrogen bonding, but again it is a small effect. In any case the hydrogen bonding can be preserved in the free maleate ion after hydrolysis. For this reason it is doubtful if the relative instability of the acetato complex can be attributed to hydrogen bonding in the dicarboxylato complexes.

There is no detectable correlation between ΔH° for the ionisation of the free acid and the hydrolysis of cobalt complex (reaction (1) above). Admittedly in these reactions there are other contributing factors besides simply the strengths of the bonds being broken, but to a considerable extent these would always be the same (e.g. the strength of the bond to H_2O in the $Co(NH_3)_5H_2O^{3+}$ ion which is formed). However such factors as enthalpies of hydration will not be the same, and since the ΔH° values are all small, any correlation of bond strengths, if it exists, is evidently obscured. The same applies to the base hydrolysis (reaction (2) above).

The kinetics of base hydrolysis of the fumarato and maleato complexes have been studied[5]. The rate constants differ by a factor of three, the maleato reacting more slowly, and both rate constants are roughly an order of magnitude less than that for the acetato complex[24]. Qualitatively therefore the rate constants follow the order of the enthalpies of the reactions, with the most exothermic reaction being fastest. However more kinetic information is needed to make a detailed comparison.

REFERENCES

1 F. Basolo and R. G. Pearson, *Mechanisms of Inorganic Reactions*, 2nd edn., Wiley, New York, 1967, Chap. 3.

2 F. Basolo and R. G. Pearson, *Mechanisms of Inorganic Reactions*, 2nd edn., Wiley, New York, 1967, Chap. 6.

3 D. K. Sebera and H. Taube, *J. Amer. Chem. Soc.*, 83 (1961) 1785.

4 E. S. Gould and H. Taube, *J. Amer. Chem. Soc.*, 86 (1964) 1318.

5 N. S. Angerman and R. B. Jordan, *Inorg. Chem.*, 6 (1967) 1376.

6 A. B. Lamb and J. P. Simmons, *J. Amer. Chem. Soc.*, 43 (1921) 2188.

7 K. B. Yatsimirsky and L. L. Pankova, *J. Gen. Chem. USSR*, 19 (1949) 569.

8 K. B. Yatsimirsky and L. L. Pankova, *Zh. Obshch. Khim.*, 18 (1948) 2051.

9 F. Basolo and R. K. Murmann, *Inorg. Synth.*, 4 (1953) 171.

10 E. S. Gould and H. Taube, *J. Amer. Chem. Soc.*, 86 (1964) 1318.
11 L. M. Jackman, R. M. Scott and R. H. Portman, *Chem. Commun.*, (1968) 1338.
12 M. B. Kennedy and M. W. Lister, *Can. J. Chem.*, 44 (1965) 1709.
13 C. W. Davies, *J. Chem. Soc.*, (1938) 2093. See also C. W. Davies, Ion Association.
14 M. V. Olson and H. Taube, *Inorg. Chem.*, 9 (1970) 2072.
15 C. Andrade and H. Taube, *Inorg. Chem.*, 5 (1966) 1087.
16 G. Svatos and H. Taube, *J. Amer. Chem. Soc.*, 83 (1961) 4172.
17 J. N. Brönsted and K. Volquartz, *Z. Phys. Chem. (Frankfurt am Main)*, 134 (1928) 97.
18 S. C. Chan and K. Y. Hui, *Aust. J. Chem.*, 21 (1968) 3061.
19 J. J. Christensen, R. M. Izatt and L. D. Hansen, *J. Amer. Chem. Soc.*, 89 (1967) 213.
20 G. A. Krestov and K. B. Yatsimirsky, *Russ. J. Inorg. Chem.*, 6 (1961) 1170.
21 U.S. National Bureau of Standards, Washington D.C., Technical Note 270-4, 1969.
22 E. J. King, *Acid-Base Equilibria.* The Macmillan Co., New York, 1965.
23 F. H. Westheimer and O. T. Benfey, *J. Amer. Chem. Soc.*, 78 (1956) 5309.
24 F. Basolo, J. G. Bergmann and R. G. Pearson, *J. Phys. Chem.*, 56 (1952) 22.