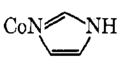
The present work provides no clear explanation of the nature of the differences in the metal–ligand bond which result in stabilization of the high-spin form when B = imidazole but not when B is a pyridine or phosphine ligand. Furthermore, comparable moments might be expected for the complexes Co^{II}(salen)(imidazole) and Co^{II}(salen)(2-methylimidazole) since they contain such similar ligands; instead, the difference between the moments of these complexes is the greatest of any pair measured. The complex Co^{II}(saloph)(imidazole) also contains the axial ligand imidazole but exhibits a high magnetic moment. Differences in the bonding of the imidazole moiety to cobalt in these complexes may be the critical factor since two distinct complexes are possible



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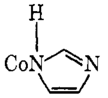

The method of preparation requires that the least soluble isomer, though not necessarily the predominant one in solution, be isolated.[22]

In view of the widespread occurrence of the benzimidazole ligand in nature, it seems worthwhile to pursue an investigation into the nature of the bonding in these complexes. Advances in X-ray crystallographic techniques make the solution of such formerly difficult problems feasible. The fortuitous existence of spin equilibria in these complexes may provide a better understanding of the bonding of these imidazole-type ligands through further study of their magnetic properties. Moreover, the dependence of the spin state of these cobalt(II) complexes on axial ligands has interesting analogs among some ferrihemoglobin and ferrimyoglobin complexes.[23]

Acknowledgments.—The authors are grateful to Professor Jack Halpern for the opportunity to conduct this research in his laboratories and for his interest in these studies. They also wish to thank Dr. Robert Maclagan (Johns Hopkins University) for helpful discussions. Support of this research by the National Science Foundation (Grant GP5385), the National Institutes of Health (Grant AM13339), and the Petroleum Research Fund (Grant 2551-C3), administered by the American Chemical Society, is gratefully acknowledged.

[23] G. Schoffa, *Advan. Chem. Phys.*, **7**, 182 (1964).

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Kinetics of Hydrolysis in Aqueous Acid of Carbonatobis(*o*-phenanthroline)- and -(2,2′-bipyridyl)cobalt(III) Ions

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The acid-catalyzed hydrolysis of the $(phen)_2CoCO_3^+$ and $(bipy)_2CoCO_3^+$ ions was found to follow the rate law $-d \ln [\text{complex}]/dt = k_0 + k_1[H^+]$ in the temperature range 50–70°. Tracer experiments using $^{18}OH_2$ indicated Co–O bond cleavage in the rate-controlling ring-opening reaction by the k_1 path. For $(phen)_2CoCO_3^+$, k_1 (25°) = $1.5 \times 10^{-4}\ M^{-1}\ sec^{-1}$, $\Delta H_1^{\ddagger} = 20.4 \pm 1.9$ kcal mol^{-1}, and $\Delta S_1^{\ddagger} = -8.6 \pm 5.1$ cal mol^{-1} deg^{-1}. The analogous values for $(bipy)_2CoCO_3^+$ are $2.2 \times 10^{-4}\ M^{-1}\ sec^{-1}$, 22.3 ± 1.7 kcal mol^{-1}, and -1.5 ± 4.8 cal mol^{-1} deg^{-1}. The k_0 values were too small to be determined accurately. The unusually small value of k_1 for these complexes is attributed to less net electron donation from the amine to cobalt(III), making Co–O bond breaking more difficult. This is supported by correlations of the rate constants with amine basicity and the pK_a of the *cis*-$N_4Co(OH_2)_2^{3+}$ complexes.

Introduction

The hydrolysis kinetics of a number of carbonato–amine–cobalt(III) systems have been studied. A review of this work was published in the past year,[1] and much of the kinetic work on acid hydrolysis has been discussed in a recent publication.[2] For tetraamine type complexes with a bidendate carbonate group, represented by $N_4CoCO_3^+$, the hydrolysis in acidic solution is found to be consistent with the reactions

$$N_4CoCO_3^+ + H_2O \xrightarrow{k_0} cis\text{-}N_4CoOHCO_3H^+ \xrightarrow{\text{fast}} \text{products} \quad (1)$$

$$N_4CoCO_3^+ + H_3O^+ \xrightarrow{k_1} cis\text{-}N_4CoOH_2CO_3H^{2+} \xrightarrow{\text{fast}} \text{products} \quad (2)$$

where the ultimate products are $N_4Co(OH_2)_2^{3+}$ and CO_2. The observed pseudo-first-order rate constant is then

$$k_{\text{obsd}} = k_0 + k_1[H^+] \quad (3)$$

For simple amine ligands such as ammonia and polydendate alkylamines these reactions have half-times of the order of seconds at 25°.[2] During the course of our work it was noticed that the hydrolysis of carbonatobis(*o*-phenanthroline)cobalt(III) was unusually slow, with a half-time of several minutes even at 60°. Slow hydrolysis of the carbonatocobalt(III) complexes of te*tb* and *trans*[14]diene has been observed previously by Kernohan and Endicott[3] and attributed to steric effects. Rate comparisons of the α- and β-trien complexes[2] indicate that ring strain in the carbonate chelate ligand is an important kinetic factor. Neither of these factors would seem to be of major significance for $(phen)_2$-

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[1] K. V. Krishnamurty, G. M. Harris, and V. S. Sastri, *Chem. Rev.*, **70**, 171 (1970).

[2] T. P. Dasgupta and G. M. Harris, *J. Amer. Chem. Soc.*, **93**, 91 (1971).

[3] J. A. Kernohan and J. F. Endicott, *ibid.*, **91**, 6977 (1969).

$CoCO_3^+$; therefore kinetic and oxygen-18 tracer studies have been carried out on the hydrolysis of this *o*-phenanthroline complex and its bipyridyl analog.

Experimental Section

Preparation of Complexes.—The carbonato-, dichloro-, and diaquobis(*o*-phenanthroline)cobalt(III) complexes were prepared by the published methods.[4,5] *Anal.* Calcd for $[(phen)_2CoCO_3]Cl \cdot 3H_2O$: C, 52.8; H, 3.9; N, 9.9; Cl, 6.2 Found: C, 50.8; H, 4.2; N, 9.4; Cl, 6.2. Calcd for *cis*-$[(phen)_2CoCl_2]Cl \cdot 3H_2O$: C, 49.8; H, 3.9; N, 9.7. Found: C, 48.2; H, 3.9; N, 9.5. Calcd for *cis*-$[(phen)_2Co(OH_2)_2]Cl_3 \cdot 2H_2O$: C, 48.3; H, 4.1; N, 9.4; Cl, 17.8. Found: C, 48.2; H, 4.3; N, 9.2; Cl, 15.8.

The *cis*-dichlorobis(2,2′-bipyridyl)cobalt(III) chloride dihydrate was prepared by the method of Vlcek.[6]

The $[(bipy)_2CoCO_3]Cl \cdot 3H_2O$ complex was prepared by dissolving 1 g of *cis*-$[(bipy)_2CoCl_2]Cl \cdot 2H_2O$ in 25 ml of warm water. One gram of anhydrous sodium carbonate (Analar) was added in portions to the violet solution which immediately turned dark red and yielded product in the form of dark red needles. Upon air drying the red needles became an orange-red powder which was recrystallized twice from redistilled water.

The perchlorate salt of the $(bipy)_2CoCO_3^+$ ion was prepared by dissolving $[(bipy)_2CoCO_3]Cl \cdot 3H_2O$ in redistilled water, adding an equivalent weight of anhydrous $NaClO_4$ (G. Frederick Smith Chemical Co.) to the solution, and collecting and air drying the orange-red precipitate. *Anal.* Calcd for *cis*-$[(bipy)_2CoCl_2]Cl \cdot H_2O$: C, 46.9; H, 3.9; N, 10.9; Cl, 20.8. Found: C, 46.7; H, 3.8; N, 10.8; Cl, 21.7. Calcd for $[(bipy)_2CoCO_3]Cl \cdot 3H_2O$: C, 48.4; H, 4.3; N, 10.8; Cl, 6.8. Found: C, 47.4; H, 4.1; N, 10.6; Cl, 6.7. Calcd for $[(bipy)_2CoCO_3]ClO_4$: C, 46.9; H, 3.0; N, 10.4; Cl, 6.6. Found: C, 45.6; H, 2.9; N, 10.7; Cl, 6.6.

Spectral Measurements.—Electronic absorption spectra of the complexes were run on a Cary 14 recording spectrophotometer. The infrared spectra of the carbonato complexes, in a KBr disk, were run on a Perkin-Elmer Model 421 infrared spectrophotometer. The nmr spectra were run on a Varian HA-100 spectrometer in D_2O with 10% *tert*-butyl alcohol as an internal reference.

Acid Hydrolysis Kinetics.—Known amounts of 1.0 *M* HCl, 2.0 *M* NaCl, and redistilled water were added to a 5-cm spectrophotometer cell. After temperature equilibration had occurred, 1.00 ml of a stock solution of complex in redistilled water was injected with a syringe through a rubber serum cap on the neck of the cell. The HCl concentration was always at least 50 times greater than the complex concentration (1.3×10^{-1} *M*). The change in absorbance with time for the *o*-phenanthroline and 2,2′-bipyridyl complexes was followed at 505 nm (Bausch and Lomb Spectronic 505 spectrophotometer) and 500 nm (Bausch and Lomb Precision spectrophotometer), respectively. The temperature of the reaction solution in the cell was controlled by water flowing through an aluminum cell block. The method of control of the water temperature has been described previously.[7]

The solution temperature was measured directly with a thermistor-bead temperature probe which was calibrated with a Hewlett-Packard quartz thermometer (2801A) and probe (2850-D) which had been factory calibrated from 0 to 100°.

All water used was redistilled from a Corning AG1b water still (Corning Glass Works, Laboratory Products Division, Corning, N. Y.). The 1.0 *M* HCl solutions were made by diluting ampoules of concentrated HCl (P-H Tamm, Bio-Rad Laboratories). The ionic strength of the solutions was always adjusted to 1.0 *M* with NaCl.

Oxygen-18 Tracer Study.—The isotopic content of the CO_2 formed during hydrolysis of the carbonate complexes in oxygen-18-enriched aqueous acid was determined. The system consisted of a water-jacketed gas bubbler fitted with a side arm closed with a serum cap, a gas dispersion tube for introduction of a nitrogen stream, and a side arm serving as a nitrogen outlet. The nitrogen stream passed from the bubbler to a Dry Ice–acetone-cooled trap filled with zinc metal to remove water vapor and then to a coil trap cooled in liquid nitrogen to trap the CO_2. The latter trap could be closed off from the nitrogen stream and evacuated on a vacuum line for subsequent transfer of the CO_2 sample.

A known weight of the solid carbonato complex was placed in the bubbler while water at the required temperature was flowing through the water jacket. Then 1.0 ml of 1.0 *M* HCl in oxygen-18-enriched water, at the required temperature, was injected onto the solid from an insulated syringe. The nitrogen stream was immediately passed through the solution and the CO_2 sample was trapped and collected using standard techniques. The isotopic content of the CO_2 from $(phen)_2CoCO_3^+$, $(bipy)_2CoCO_3^+$, and $(en)_2CoCO_3^+$ (as a standard) was determined at 71° for reaction times of 5–10 min and at 25° for a reaction time of 31 min.

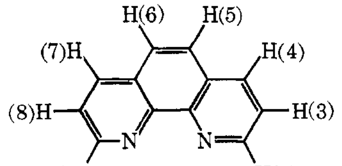
Oxygen-18-enriched water (1.7% enriched) was used as obtained from Bio-Rad Laboratories. The HCl solution was made by dilution of the concentrated acid with isotopically enriched water. The isotope analyses were carried out on a CEC Model 21-614 mass spectrometer. The intensity ratio of the 46:44 mass peaks was determined from the heights of the appropriate peaks. The ratio of 46:44 peaks was found to be 4.01 (±0.05) $\times 10^{-3}$ in a sample of normal isotopic content.

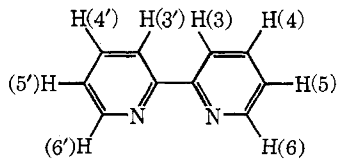
Results

Characterization of Complexes.—The complexes studied in this work have been characterized by C, H, and N analyses and visible, infrared, and nmr spectroscopy. The positions of maxima and molar extinction coefficients for the visible spectrum are summarized in Table I. There is generally excellent agreement with previous work, except for the extinction coefficient of $(bipy)_2Co(OH_2)_2^{3+}$. The difference in reported values is not just due to a medium effect and no explanation can be offered at present.

The infrared spectra of $((phen)_2CoCO_3)Cl \cdot 3H_2O$ and $((bipy)_2CoCO_3)Cl \cdot 3H_2O$ have been recorded in KBr disks. The infrared absorptions can be readily assigned by analogy to previous work on chelated carbonate[8,9] and bipyridyl and *o*-phenanthroline complexes.[10]

The proton nmr spectra of $(phen)_2CoCO_3^+$ and $(bipy)_2CoCO_3^+$ shown in Figures 1 and 2 confirm the cis-chelated structure of the carbonate complexes. The spectral assignments are based on the numbering system given below





As has been noted previously[11,12] the halves of the chelate will be different in the bis complex. For example in *o*-phenanthroline, one half (say the 2,3,4,5 half) is trans to a carbonate oxygen and has the 2 proton over the center of a pyridine ring of the other *o*-

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[4] A. V. Ablov, *Russ. J. Inorg. Chem.*, **6**, 157 (1961).

[5] A. V. Ablov and D. M. Palade, *ibid.*, **6**, 306 (1961).

[6] A. A. Vlcek, *Inorg. Chem.*, **6**, 1425 (1967).

[7] D. J. Francis and R. B. Jordan, *J. Amer. Chem. Soc.*, **91**, 6626 (1969).

[8] K. Nakamoto, J. Fujita, S. Tanaka, and M. Kobayashi, *ibid.*, **79**, 4904 (1957).

[9] J. Fujita, A. E. Martell, and K. Nakamoto, *J. Chem. Phys.*, **36**, 339 (1962).

[10] A. A. Schilt and R. C. Taylor, *J. Inorg. Nucl. Chem.*, **9**, 211 (1959).

[11] R. E. Desimone and R. S. Drago, *Inorg. Chem.*, **8**, 2517 (1969).

[12] G. M. Bryant and J. E. Ferguson, *Aust. J. Chem.*, **24**, 441 (1971).

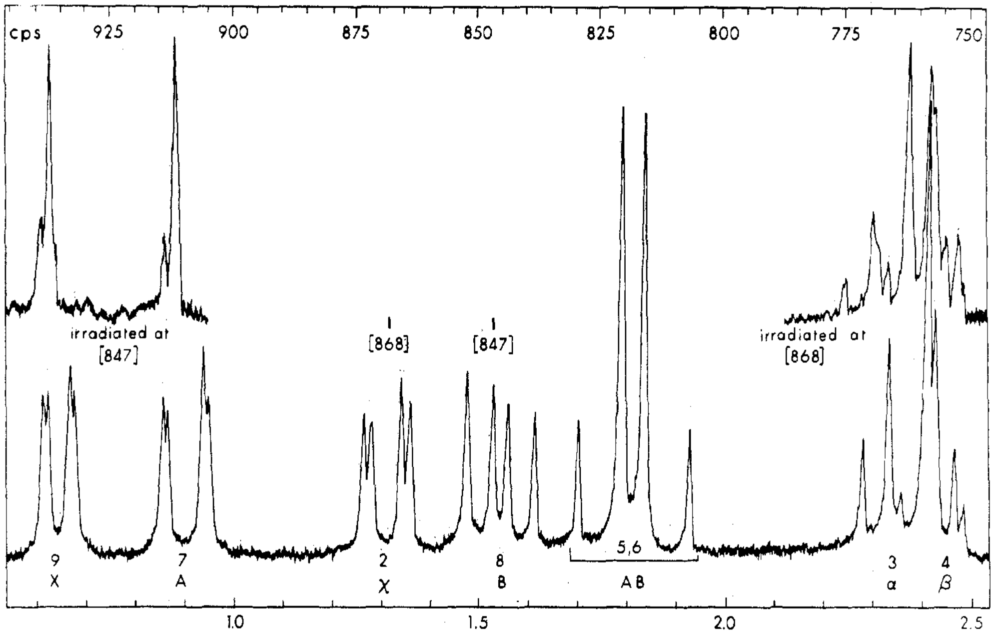

Figure 1.—The 100-MHz nmr spectrum of $((phen)_2CoCO_3)Cl\cdot 3H_2O$ in D_2O with 10% *tert*-butyl alcohol as an internal reference. Chemical shifts are given relative to TMS. The *tert*-C_4H_9OH–TMS separation was determined to be 120.8 Hz.

TABLE I

POSITION (λ) AND MOLAR EXTINCTION COEFFICIENTS (ε) OF MAXIMA IN THE VISIBLE SPECTRA OF SOME COBALT(III) COMPLEXES

Complex ion	λ_{max}, nm	ϵ_{max}, M^{-1} cm^{-1}
$(phen)_2CoCO_3^+$	509^a (510^c)	109^a (106^c)
cis-$(phen)_2Co(OH_2)_2^{3+}$	500^b (500^c)	63^b (60^c)
$(bipy)_2CoCO_3^+$	504^a (504^d)	116^a (110^d)
cis-$(bipy)_2Co(OH_2)_2^{3+}$ ^{e}	490 (489^f)	60 (48^f)

[a] In 1.0 M NaCl; this work. [b] In 1.0 M HCl; this work. [c] A. V. Ablov and D. M. Palade *Russ. J. Inorg. Chem.*, **6**, 306 (1961). [d] A. A. Vlcek, *Inorg. Chem.*, **6**, 1425 (1967). [e] Produced by acid hydrolysis of $(bipy)_2CoCO_3^+$ in 1.0 M $HClO_4$. [f] D. M. Palade, *Russ. J. Inorg. Chem.*, **14**, 231 (1969); measured in redistilled water.

phenanthroline, while the other half is trans to a nitrogen and the 9 proton lies over the carbonate ligand. The 2 proton is strongly shifted upfield due to the ring current effect as is observed in Figure 1. The spectrum of $(phen)_2CoCO_3^+$ was assigned with the aid of spin-decoupling experiments and usual methods for an ABX system.[13,14] The resonances for protons 2, 3, 4, 7, 8, and 9 are centered at τ 1.32, 2.36, 2.44, 0.90, 1.58, and 0.65, respectively. The coupling constants (Hz) are $J_{2,3} = 4.2$, $J_{2,4} = 1.3$, $J_{3,4} = 8.5$, $J_{8,9} = 5.5$, $J_{7,9} = 1.1$, and $J_{7,8} = 8.2$. The coupling constants are all similar to those observed in the *o*-phenanthroline molecule.[15]

The spectrum of $(bipy)_2CoCO_3^+$ was not sufficiently spread out to permit a detailed assignment. However, spin decoupling and analogy to *o*-phenanthroline showed that the positions are approximately as shown in Figure 2. The 3′, 4′, 5′, and 6′ protons are on the part of the ligand which is over another bipyridine and therefore the 6′ proton is shifted to high field. It may be noted that the spectrum of $(bipy)_2CoCO_3^+$ is similar qualitatively to that of $(bipy)_2IrCl_2^+$ [11] except that the 5′ proton is at higher field than the 6′ in the latter complex.

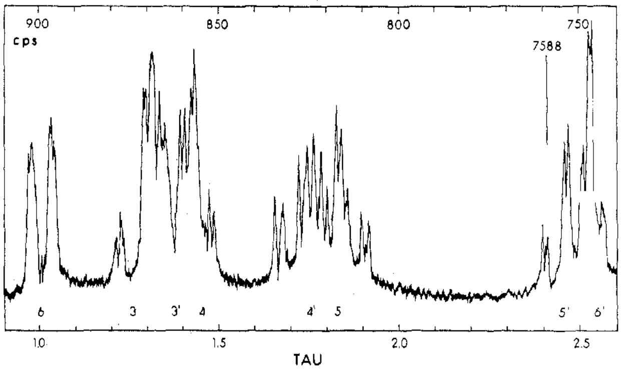

Figure 2.—The 100-MHz nmr spectrum of $((bipy)_2CoCO_3)$-$Cl\cdot 3H_2O$ in D_2O. The calibration line is 638 Hz from the *tert*-butyl alcohol internal standard and 758.8 Hz from TMS.

Kinetic Study.—Several lines of evidence show that the reaction being studied is of the general type

$$N_4CoCO_3^+ + H_2O \xrightarrow{H^+} cis\text{-}N_4Co(OH_2)_2^{3+} + CO_2 \qquad (4)$$

where N_4 is $(phen)_2$ or $(bipy)_2$. The oxygen-18 tracer studies discussed below show that a large amount of CO_2 is given off during the reaction. In addition the visible spectra of the products correspond to those of the diaquo complex. Hydrolysis of $(bipy)_2CoCO_3^+$ in 1 M $HClO_4$ produces a product with an extinction coefficient of 56.5 M^{-1} cm^{-1} at 500 nm, compared to a value of 57.0 for the product from hydrolysis in 1 M HCl. Hydrolysis of $phen_2CoCO_3^+$ in 1 M HCl gives a product with an extinction coefficient of 49 M^{-1} cm^{-1} at 504 nm compared to a value of 48.1 M^{-1} cm^{-1} for *cis*-$(phen)_2Co(OH_2)_2Cl_3\cdot 3H_2O$ dissolved in 1 M HCl. The cis configuration of the latter was established from its nmr spectrum and seems to be strongly preferred by all bis-*o*-phenanthroline and bis-bipyridyl complexes.[16]

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[13] V. M. S. Gil, *Mol. Phys.*, **9**, 97 (1965).

[14] H. J. Bernstein, J. A. Pople, and W. G. Schneider, *Can. J. Chem.*, **35**, 65 (1957).

[15] H. Rosenberger, M. Pettig, K. Madeja, and G. Klose, *Ber. Bunsenges. Phys. Chem.*, **78**, 847 (1968).

[16] J. G. Gibson, R. Laird, and E. D. McKenzie, *J. Chem. Soc. A*, 2089 (1969).

The observed pseudo-first-order rate constants, k_{obsd}, were determined from the normal log $(A_t - A_\infty)$ *vs.* time plots. A_t and A_∞ refer to the solution absorbance at any time t and at complete reaction, respectively. The dependence of k_{obsd} on $[H^+]$ for the acid hydrolysis of both complexes is given by eq 3. The observed rate constants for the acid hydrolysis of each complex, at each temperature, were fitted to eq 1 using a least-squares computer program.[17] Figure 3 shows the dependence of k_{obsd} on $[H^+]$ at 69.3° for the acid hydrolysis of the $(bipy)_2CoCO_3^+$ ion, as well as the straight line calculated from the best-fit values of k_0 and k_1. Table II gives the experimental value of k_{obsd} and the value of k_{obsd} calculated from the best-fit values of k_0 and k_1 at 50.0° for the acid hydrolysis of the $(phen)_2CoCO_3^+$ ion. Tables III and IV give the best-fit values of k_0 and k_1, their 95% confidence limits, and the activation parameters and error limits determined from a transition-state plot of log k_1/T *vs.* $1/T$, for the acid hydrolyses of the $(bipy)_2CoCO_3^+$ and $(phen)_2CoCO_3^+$ ions, respectively.

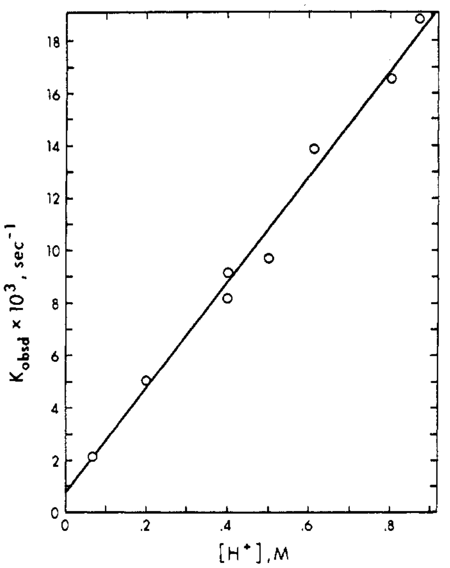

Figure 3.—Variation of k_{obsd} with $[H^+]$ for the hydrolysis of $(bipy)_2CoCO_3^+$ in aqueous hydrochloric acid, at 69.3°, and an ionic strength of 1.0 *M* adjusted with NaCl.

TABLE II

KINETIC RESULTS FOR THE HYDROLYSIS OF $(phen)_2CoCO_3^+$ IN HCl, AT 50°, IONIC STRENGTH 1.0 *M* (NaCl)

[HCl], *M*	10^3k_{obsd}, sec^{-1}		[HCl], *M*	10^3k_{obsd}, sec^{-1}	
	Obsd	Calcd[a]		Obsd	Calcd[a]
0.0666	0.133	0.142	0.500	0.963	0.867
0.0666	0.123	0.142	0.500	0.825	0.867
0.127	0.230	0.242	0.500	0.905	0.867
0.200	0.403	0.365	0.600	1.00	1.03
0.200	0.418	0.365	0.600	1.00	1.03
0.200	0.398	0.365	0.715	1.10	1.23
0.269	0.423	0.480	0.715	1.25	1.23
0.287	0.550	0.511	0.715	1.28	1.23
0.400	0.626	0.700	0.800	1.52	1.37
0.400	0.666	0.700	0.800	1.28	1.37
0.483	0.834	0.839			

[a] Calculated from eq 1 using the least-squares best-fit values of k_0 and k_1, given in Table IV.

TABLE III

SPECIFIC RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE ACID HYDROLYSIS OF $(bipy)_2CoCO_3^+$[a,b]

Temp, °C	10^4k_0,[c] sec^{-1}	10^2k_1, M^{-1} sec^{-1}
52.0	0.327 ± 2.03	0.343 ± 0.033
60.0	4.08 ± 3.40	0.931 ± 0.067
69.3	6.50 ± 10.25	2.03 ± 0.187

$\Delta H^\ddagger = 22.3 \pm 1.7$ kcal mol^{-1}
$\Delta S^\ddagger = -1.50 \pm 4.8$ cal mol^{-1} deg^{-1}

[a] Ionic strength 1.0 *M* (NaCl). [b] Errors quoted are 95% confidence limits. [c] No activation parameters are given because of the large errors in the k_0 values.

TABLE IV

SPECIFIC RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE ACID HYDROLYSIS OF $(phen)_2CoCO_3^+$[a,b]

Temp, °C	10^4k_0,[c] sec^{-1}	10^2k_1, M^{-1} sec^{-1}
50.0	0.309 ± 0.605	0.167 ± 0.012
60.5	1.68 ± 1.31	0.514 ± 0.052
71.1	10.4 ± 8.88	1.23 ± 0.147

$\Delta H^\ddagger = 20.4 \pm 1.9$ kcal mol^{-1}
$\Delta S^\ddagger = -8.6 \pm 5.1$ cal mol^{-1} deg^{-1}

[a] Ionic strength 1.0 *M* (NaCl). [b] Errors quoted are 95% confidence limits. [c] No activation parameters are given because of the large errors in the k_0 values.

For both of the complex acid hydrolyses, the 95% confidence limits on the parameters show that the values of k_0 are not necessarily greater than zero. For this reason no transition-state activation parameters were calculated for k_0. However, since the best-fit values of k_0 are always positive, it is felt that the k_0 term in eq 1 is real, although inaccurately determined.

Oxygen-18 Tracer Study.—These results have been expressed in terms of the parameter *R*, defined as the ratio of the intensities of the mass 46 to mass 44 peaks in the mass spectrum of CO_2. The values R_0 and R_∞ refer to the ratios for normal unenriched-in-^{18}O carbon dioxide and for the ^{18}O-enriched solvent, respectively. *F*, the fraction of enrichment in a CO_2 sample, is defined by $F = (R - R_0)/(R_\infty - R_0)$.

TABLE V

TRACER EXPERIMENTS ON THE BOND BREAKING DURING THE ACID HYDROLYSIS OF $(bipy)_2CoCO_3^+$ AND $(phen)_2CoCO_3^+$ IN 1.0 *M* HCl[a]

Complex	Temp, °C	*R*	*F*
$(en)_2CoCO_3^+$	71	0.01032	0.302
$(en)_2CoCO_3^+$	71	0.00768	0.189
$(bipy)_2CoCO_3^+$	71	0.00806	0.208
$(phen)_2CoCO_3^+$	71	0.00973	0.291
$(en)_2CoCO_3^+$	25	0.00528	0.0690
$(en)_2CoCO_3^+$	25	0.00582	0.0960
$(bipy)_2CoCO_3^+$	25	0.00441	0.0258
$(phen)_2CoCO_3^+$	25	0.00422	0.0164

[a] The CO_2 was collected for 10 min in runs at 71° and for 31 min in runs at 25°.

The results of the tracer experiments are given in Table V. The acid hydrolysis of $(NH_3)_4CoCO_3^+$ is known[18] to go with no incorporation of solvent oxygen in the evolved CO_2. Since the $(en)_2CoCO_3^+$ ion is assumed to undergo acid hydrolysis by the same mech-

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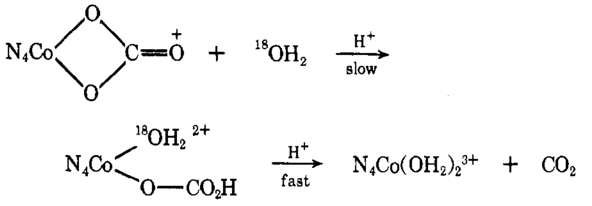
[17] L. L. Rines, J. A. Plambeck, and D. J. Francis, "ENLLSQ Reprogrammed," Program Library, Department of Chemistry, University of Alberta, 1970.

[18] F. A. Posey and H. Taube, *J. Amer. Chem. Soc.*, **75**, 4099 (1953).

anism, a low value of F for the $(en)_2CoCO_3^+$ is expected. The results in Table V show that there is a considerable amount of method-induced exchange at 71°. This probably results from CO_2 exchange with the oxygen-18-enriched solvent before it is swept out of the solution by the nitrogen stream. At 25° the induced exchange is greatly reduced and the CO_2 evolved contains essentially no oxygen derived from the solvent.

Discussion

The results of the tracer studies and a consideration of previous work indicates that the acid-catalyzed reaction proceeds according to



(5)

The tracer results in this work show that the first step occurs with Co–O bond breaking. The second step is expected to be fast since the rate constant is ~1.3 sec^{-1} at 25° for the analogous reaction of $(NH_3)_5CoCO_3H^{2+}$ [19] and $(tren)CoOH_2CO_3H^{2+}$.[2] Previous tracer studies on $(NH_3)_5CoCO_3^+$ [20] and $(NH_3)_4CoCO_3^+$ [18] provide evidence that the second reaction proceeds with O–C bond breaking. The kinetic parameters for the k_1 path for the complexes studied to date are collected in Table VI.

TABLE VI

RATE PARAMETERS FOR THE ACID-CATALYZED HYDROLYSIS OF VARIOUS $N_4CoCO_3^+$ IONS AT 25°

N_4	k_1,[a] M^{-1} sec^{-1}	$\Delta H_1^{\ddagger}$, kcal mol^{-1}	$\Delta S_1^{\ddagger}$, eu	Av pK_a of amine ligand[c]	First pK_a of $N_4Co(OH_2)_2^{3+}$
$(NH_3)_4$	1.5	15.3	−6.8	9.3 (1)[d,e]	6.0[d,i]
$(en)_2$	0.6	13.8	−7.4	8.6 (2)[d,f]	6.1[i,j]
$(pn)_2$	0.5	14	−13	8.5 (2)[d,g]	...
$(tn)_2$	0.8	12	−19	9.7 (2)[d,f]	...
tren	2.0	11.1	−20.0	...	...
cis-en$(NH_3)_2$	0.9	16.0	−4.0	...	...
trans-en$(NH_3)_2$	8.9	10.0	−20.0	...	...
α-trien	5.2	15.0	−5.0	7.3 (4)[d,f]	5.3[k]
β-trien	0.2	17.0	−5.0		
trans[14]diene	8×10^{-3}	24	...	...	...
tet*b*	10^{-4}	...	...	6.3 (4)[h]	...
$(phen)_2$	1.5×10^{-4} [b]	20.4	−8.6	5.0 (1)[d,f]	4.7[l]
$(bipy)_2$	2.2×10^{-4} [b]	22.3	−1.5	4.5 (1)[d,f]	4.5[m]

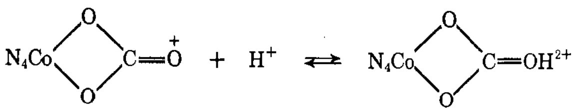
[a] Original references to previous work are given in Table VII of T. P. Dasgupta and G. M. Harris, *J. Amer. Chem. Soc.*, **93**, 91 (1971). [b] This work; obtained by extrapolation of log (k_1/T) *vs.* T^{-1} plots. [c] Number in parentheses is the number of successive pK values which were averaged. [d] L. G. Sillén and A. E. Martell, Ed., *Chem. Soc., Spec. Publ.*, **No. 17** (1964). [e] At 20° corrected to zero ionic strength. [f] At 20° in 0.1 M $NaNO_3$. [g] At 25° in 1.0 M KCl. [h] N. F. Curtis, *J. Chem. Soc.*, 2644 (1964). [i] At 25° in 1.0 M $NaNO_3$. [j] J. Bjerrum and S. E. Rasmussen, *Acta Chem. Scand.*, 6, 1265 (1952). [k] C. J. Hawkins, A. M. Sargeson, and G. H. Searle, *Aust. J. Chem.*, **17**, 598 (1964); measured at 20° in 0.1 M $NaClO_4$. [l] A. V. Ablov and D. M. Palade, *Russ. J. Inorg. Chem.*, 6, 567 (1961); measured at 25° in 1.0 M KNO_3. [m] D. M. Palade, *ibid.*, 14, 231 (1969); measured at 25° in 1.0 M KNO_3.

The factors affecting the rate of carbonate chelate ring opening have been discussed in several recent papers by Harris and coworkers.[2,21] The rate constant k_1 is "normally" in the range of 1-2 M^{-1} sec^{-1} at 25°. Larger values of k_1 for *trans*-$(NH_3)_2enCoCO_3^+$ and α-$trienCoCO_3^+$ have been attributed to greater ring strain of the carbonate chelate induced by the requirements of the amine chelate ring trans to the carbonate ligand. These arguments are qualitatively supported by the crystal structures of $Co(en)_3^{3+}$ [22] and α-Co(trien)$ClNH_3^{2+}$ [23] which indicate an N–Co–N angle of 87.4 and 87.3°, respectively, compared to the value of 94.5° observed in $(NH_3)_4CoCO_3^+$.[24]

However this ring strain factor cannot be used to explain carbonate–chelate ring-opening rates which are slower than that of the tetraammine complex. For example in β-Co(trien)$ClOH_2^{2+}$ the appropriate N–Co–N angle is 93.1° and the ring strain argument would predict a rate about the same or slightly faster than for $(NH_3)_4CoCO_3^+$. In fact the k_1 value is ~8 times smaller, at 25°, for the β-trien complex. A crystal structure determination of the $(bipy)_2CoCO_3^+$ complex is in progress, but the structure of $(phen)_2CoCl_2^+$ [25] indicates that the N–Co–N angle trans to the chloro ligands is 94°, and it seems unlikely that this will increase markedly as would be required to explain the small hydrolysis rate of $(bipy)_2CoCO_3^+$ and $(phen)_2CoCO_3^+$.

Previous arguments that steric effects might explain the small k_1 values do not seem generally to be tenable. Models do not indicate any steric restrictions on the bipyridyl or *o*-phenanthroline complexes studied in this work. The recent structure determination of Ni(tet*b*)$O_2CCH_3^+$ [26] does not reveal any significant blocking of the chelated acetate ligand by the tet*b* ligand. Therefore none would be expected in the Co(tet*b*)CO_3^+ ion although its acid hydrolysis rate is only 10^{-4} M^{-1} sec^{-1} at 25°.[3]

It is of interest to note that, except for the two cases where ring strain explains the large values of k_1, the rates can be correlated with the basicity of the amine ligands. The average pK values are given along with the kinetic parameters in Table VI. The correlation is rather crude inevitably because of the necessity of taking average values of pK's for the polydendate amines but it does provide a qualitative explanation for the low k_1 values for the β-trien, *trans*[14]diene, $(bipy)_2$, and $(phen)_2$ systems. This correlation may be rationalized if it is assumed that the more basic amines are better electron donors to cobalt(III) and facilitate Co–O bond breaking by the k_1 path. It is possible also that the acid-catalyzed path involves a preliminary protonation equilibrium, possibly but not necessarily on the carbonyl oxygen, such as



(6)

This protonation would also be favored by the better electron-donor amine ligands since they would reduce

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(19) T. P. Dasgupta and G. M. Harris, *J. Amer. Chem. Soc.*, **90**, 6360 (1968).

(20) (a) J. P. Hunt, A. C. Rutenberg, and H. Taube, *ibid.*, **74**, 268 (1952); (b) C. A. Bunton and D. R. Lewellyn, *J. Chem. Soc.*, 1692 (1953).

(21) R. J. Dobbins and G. M. Harris, *J. Amer. Chem. Soc.*, **92**, 5104 (1970).

(22) K. Nakatsu, *Bull. Chem. Soc. Jap.*, **30**, 158 (1957).

(23) M. Dwyer and I. E. Maxwell, *Inorg. Chem.*, **9**, 1459 (1970).

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(25) A. V. Ablov, A. Yu. Kon, and T. I. Malinovskii, *Dokl. Chem.*, **167**, 410 (1966).

(26) P. O. Whimp, M. F. Bailey, and N. F. Curtis, *J. Chem. Soc. A*, 1956 (1970).

inductive electron withdrawal from the CO_3^{2-} ligand by the cobalt.

A possibly more direct measure of the effect of the amine ligand may be gained from the pK_a values of the aquo species, $N_4Co(OH_2)_2^{3+}$. The more strongly electron-donating amines should make the coordinated water molecule less acidic. These pK_a values also are given in Table VI and generally show the expected trend with amine pK and hydrolysis rate. It is concluded from these correlations that the electron-donor variations of the amines are much more important than steric effects in explaining the large variation in the acid hydrolysis rate constants (k_1) for the $N_4CoCO_3^+$ systems.

It has been proposed by Gatehouse, *et al.*,[27] that the C=O stretching frequency in chelated carbonate complexes might be used as a measure of the M–O bond energy, a higher stretching frequency correlating with a stronger M–O bond. This correlation has been applied recently by Farago, Keefe, and Mason[28] to the $(phen)_2CoCO_3^+$ complex which has ν(C=O) 1650 cm^{-1} compared to 1613 and 1593 cm^{-1} in $(en)_2CoCO_3^+$ and $(NH_3)_4CoCO_3^+$, respectively. A value of 1632 cm^{-1} has been observed in our work for $(bipy)_2CoCO_3^+$, and Endicott, *et al.*,[29] give values of 1665 and 1597 cm^{-1} for the *trans*[14]diene and tet*b* complexes. Comparison of the ν(C=O) values and rate constants (k_1) shows that a qualitative correlation does exist except for the tet*b* complex. The larger $\Delta H_2^{\ddagger}$ of $(NH_3)_4CoCO_3^+$ compared to that of $(en)_2CoCO_3^+$ and of $(bipy)_2CoCO_3^+$ compared to that of $(phen)_2CoCO_3^+$ would not be anticipated from the ν(C=O) values however. Also the compilation of ν(C=O) values in ref 1 shows that the value is affected by anion and hydrogen-bonding effects and that *trans*-$(NH_3)_2enCoCO_3^+$ and $trienCoCO_3^+$ complexes do not conform to the expectations of Farago, *et al.*

Although the k_0 values determined here are quite inaccurate, they do provide an upper limit which indicates that k_0 is $\sim 10^2$ times smaller in the $(phen)_2CoCO_3^+$ and $(bipy)_2CoCO_3^+$ systems than in the more normal cases such as $(en)_2CoCO_3^+$. It appears that the k_0 values roughly parallel the k_1 values. This implies that the k_0 path also proceeds with Co–O bond breaking, a point which has yet to be established. The greater sensitivity of k_1 to changes in the amine ligands may be rationalized if it is assumed that both the protonation equilibrium (eq 6) and bond breaking are involved in the k_1 path, but only bond breaking will be important for the k_0 path.

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[27] B. M. Gatehouse, S. E. Livingston, and R. S. Nyholm, *J. Chem. Soc.*, (1958).

[28] M. E. Farago, I. M. Keefe, and C. F. V. Mason, *ibid.*, *A*, 3194 (1970).

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Iridium(I) and Iridium(III) Complexes with *cis*-Vinylenebis(diphenylphosphine)

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The preparation of new four- and five-coordinated complexes of iridium(I) and six-coordinated complexes of iridium-III with *cis*-vinylenebis(diphenylphosphine) (dp) is reported. The properties of the compounds are discussed with regard to the presence of the double bond in the dp ligand, which results in a better π acceptor than 1,2-bis(diphenylphosphino)ethane (DP).

Introduction

It is well known that several transition metal complexes having particularly "soft" ligands are apt to coordinate small molecules, such as H_2, O_2, CO, etc., in a reversible way. Some new useful complexes in this regard are those of formula $[IrY(dp)_2]X$ (Y = CO, H_2, O_2, HCl, HBr, HI; X = Cl, Br, I, ClO_4, BPh_4; dp = *cis*-vinylenebis(diphenylphosphine), $Ph_2PCH{=}CHPPh_2$) and $[Ir(dp)_2]X$, which we have recently synthetized. These chelate complexes behave somewhat differently from the analogous compounds containing the saturated diphosphine-1,2-bis(diphenylphosphino)ethane $C_2H_4(PPh_2)_2$ (DP).[1] This different behavior is attributed to the double bond present in the dp ligand.

Experimental Section

All reactions were carried out under a nitrogen atmosphere. Infrared spectra were obtained with a Perkin-Elmer spectrometer Model 337. Melting points are uncorrected. Analytical data are reported in Table I. Infrared spectral data are reported in Table II. The diphosphine was prepared previously as reported.[2]

Carbonylbis(*cis*-vinylenebis(diphenylphosphine))iridium(I) Chloride, $[Ir(CO)\{C_2H_2(Ph_2P)_2\}_2]Cl$.—(a) A solution of $[IrCl(CO)(Ph_3P)_2]$ (1.37 g, 1.75 mmol) in degassed benzene (120 ml) was treated, under stirring, with a solution of dp (1.45 g, 3.66 mmol) in benzene (5 ml). The mixture was stirred for several hours. The yellow-green precipitate was filtered, washed with benzene, and crystallized from acetone–benzene (2:1) in petroleum ether (bp 60–80°).

(b) An acetone–benzene solution of $[Ir\{C_2H_2(Ph_2P)_2\}_2]Cl$ was saturated with carbon monoxide. The reaction occurred instantaneously and the carbonyl compound was precipitated by addition of petroleum ether. If $[Ir(dp)_2]Cl$ was allowed to react in the solid state with carbon monoxide, its conversion to carbonyl compound was very slow, but complete within 10 days. The corresponding carbonyl bromide, iodide, perchlorate, and tetraphenylborate complexes were obtained from the chloride by exchange with the appropriate salt in water–ethanol solution.

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[1] L. Vaska and D. L. Catone, *J. Amer. Chem. Soc.*, **88**, 5324 (1966).

[2] A. M. Aguiar and D. J. Daigle, *ibid.*, **86**, 2299 (1964).