equivalent at room temperature. The mechanism of this process is assumed to be the same as that proposed for the butadieneiron tricarbonyl system.[4]

If PF_3 and CO are quite similar as ligands, the apical and basal positions should be occupied in a nearly random fashion. The cyclohexadiene system contrasts with the butadiene system with regard to the occupation of these sites. In the mono- and diphosphines of the butadiene system, PF_3 prefers to occupy the apical site and only the isomers based on that preference are observed. For the cyclohexadiene system, all possible isomers are detected. It is interesting that the carbonyl stretching force constants calculated for both systems predict this site preference. In butadieneiron tricarbonyl, K_1 is at least 0.15 mdyn/Å greater than K_2 indicating that the two types of carbonyl sites are not equivalent. In cyclohexadieneiron tricarbonyl, where the two force constants are essentially equal, the two types of sites are more nearly equivalent. For these types of systems, PF_3 and CO are apparently not equal in their bonding ability. Other dieneiron tricarbonyl systems are currently being studied in an effort to determine (1) whether this type of prediction can be extended to other systems, (2) the reasons for the different behavior of different dienes, and (3) the effect of different dienes on the intramolecular process.

Acknowledgment.—The authors wish to thank the AEC and NSF (GP-20276) for financial assistance during this project.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
THE UNIVERSITY OF CHICAGO, CHICAGO, ILLINOIS 60637

Magnetic Spin Equilibria in Some New Five-Coordinate Schiff Base Complexes of Cobalt(II)

BY LUIGI G. MARZILLI*[1] AND PATRICIA A. MARZILLI

Received April 27, 1971

Solid-state, room-temperature magnetic susceptibility data for six new complexes of the type $Co^{II}(salen)B$ (where salen = *N,N'*-bis(salicylidene)ethylenediamino and B = imidazole, 2-methylimidazole, benzimidazole, 5,6-dimethylbenzimidazole, 3-iodopyridine, and 3,5-lutidine) and one new complex of the type $Co^{II}(saloph)B$ (where saloph = *N,N'*-bis(salicylidene)-*o*-phenylenediamino and B = imidazole) are reported. The room-temperature moments lie between 1.9 and 3.5 BM, and the results are interpreted as arising from $^4A''$ to $^2A'$ spin equilibria. The anomalous temperature dependence of the magnetic susceptibility of $Co^{II}(salen)$(5,6-dimethylbenzimidazole) is that expected for such equilibria. This conclusion is also applicable to complexes of the type $Co^{II}(saloph)B$ (where B = pyridine, 3,4-lutidine, and 1-methylimidazole) in methylene chloride solution. The results afford a reasonable explanation for the dependence on B of the "outer-sphere" reduction of nitrobenzyl halides by these complexes.[2,3]

Introduction

Several low-spin, five-coordinate cobalt(II) d^7 complexes have been shown[4–6] to undergo the reaction with organic halides (RX)

$$2Co^{II} + RX \longrightarrow Co^{III}X + Co^{III}R \qquad (1)$$

Rates of reaction 1 for a large variety of organic halides and several complexes (*e.g.*, $Co^{II}(CN)_5{}^{3-}$ and $Co^{II}(DH)_2B$, where B = pyridine, triphenylphosphine, etc., and DH_2 = dimethylglyoxime) have been studied by Halpern and coworkers.[4–6] The mechanism (eq 2 and 3) advanced to explain the data involves halogen abstraction[2] as the rate-determining step.

$$Co^{II} + RX \longrightarrow Co^{III}X + R\cdot \qquad (2)$$

$$R\cdot + Co^{II} \longrightarrow Co^{III}R \qquad (3)$$

Extension of these reactions to other cobalt(II) complexes, principally of the type *N,N'*-bis(salicylidene)-ethylenediamino(1-methylimidazole)cobalt(II) (Co^{II}(salen)(1-methylimidazole)) led to the discovery of a new class of reactions[2] involving "outer-sphere" electron transfer (eq 4–8) when RX is a ring-substituted nitrobenzyl halide. When 1-methylimidazole is replaced by pyridine, however, the reduction occurs *via* the more usual halogen atom transfer pathway.[3] The reasons for the unusual difference in reaction mechanism for such apparently similar ligands are not clear.

$$Co^{II}(salen) + B \overset{K_1}{\rightleftharpoons} Co^{II}(salen)B \qquad (4)$$

$$Co^{II}(salen)B + B \rightleftharpoons Co^{II}(salen)B_2 \qquad (5)$$

$$Co^{II}(salen)B_2 + RX \xrightarrow{slow} Co^{III}(salen)B_2 + RX\cdot^- \qquad (6)$$

$$RX\cdot^- \xrightarrow{fast} R\cdot + X^- \qquad (7)$$

$$R\cdot + Co^{II}(salen)B \xrightarrow{fast} Co^{III}(salen)BR \qquad (8)$$

Preliminary studies of the magnetic susceptibility of methylene chloride solutions of Co^{II}(salen) and Co^{II}(saloph) (where saloph = *N,N'*-bis(salicylidene)-*o*-phenylenediamino) in the presence of ligands such as pyridine and 1-methylimidazole revealed magnetic moments intermediate between low spin (*ca.* 2 BM) and high spin (*ca.* 4–5 BM). Those complexes which reacted by the outer-sphere mechanism had higher moments than those which favored halogen abstraction.

---

[1] To whom correspondence should be addressed at the Chemistry Department, The Johns Hopkins University, Baltimore, Md. 21218.

[2] L. G. Marzilli, P. A. Marzilli, and J. Halpern, *J. Amer. Chem. Soc.*, **92**, 5752 (1970).

[3] L. G. Marzilli, P. A. Marzilli, and J. Halpern, *ibid.*, **93**, 1374 (1971).

[4] J. Halpern and J. P. Maher, *ibid.*, **86**, 2311 (1964); **87**, 5361 (1965).

[5] P. W. Schneider, P. F. Phelan, and J. Halpern, *ibid.*, **91**, 77 (1969).

[6] P. B. Chock and J. Halpern, *ibid.*, **91**, 582 (1969).

In addition, the magnetic susceptibility exhibited an anomalous temperature dependence which could be regarded as resulting from magnetic equilibria. The accuracy of the data was limited, however, by equilibria such as (4) and (5). Several new complexes as well as one known complex of the form Co^{II}(salen)B were prepared and isolated for the more precise investigations described below.

Experimental Section

Magnetic susceptibilities of the solid samples were measured by the Faraday method, using a Cahn RG electrobalance equipped with a Sargent SR recorder and an Alpha 7500 electromagnet operated at 5–9 A. The latter was mounted on a hydraulic lift which was utilized in conjunction with a cathetometer to maintain the position of the sample relative to the magnet constant. Temperatures were determined (±0.1°) with a United Systems Corp. Model 564 digital thermocouple thermometer. Readings were taken after the sample had equilibrated under vacuum, *i.e.*, when the change in weight on evacuation had ceased and a constant deflection was observed on applying the field after various time intervals. Diamagnetic corrections for the containers, which were either a quartz bucket or a shortened, capped nmr tube (for air-sensitive compounds), were determined over the temperature ranges studied. The instrument was calibrated using $HgCo(SCN)_4$ and χ_g calculated by utilizing the following relationship

$$\frac{16.44}{\chi_g} = \frac{\dfrac{\text{deflection of tube} - \text{deflection of HgCo(SCN)}_4}{\text{weight of HgCo(SCN)}_4}}{\dfrac{\text{deflection of tube} - \text{deflection of complex}}{\text{weight of complex}}}$$

The value of the numerator was determined several times with good agreement (±1%) and an average value was used in determining χ_g. Magnetic moments were calculated using the expression $\mu = 2.84\sqrt{\chi_M T}$, after diamagnetic corrections had been applied by the method of Figgis and Lewis.[7]

Magnetic moments in solution were determined from the chemical shift difference between the methylene chloride signal in the tube and in a concentric capillary by applying Evans' method.[8] The temperature in the probe of the Varian Associates Model A-60A nmr spectrometer was established by utilizing the known temperature dependence of the chemical shift difference in the spectrum of methanol. Allowances were made for the variation of the volume of the solution with temperature and for the effects of excess ligand.

All reactions and manipulations were carried out in a nitrogen-filled glove bag with deoxygenated solvents (reagent grade) and reagents, unless stated otherwise. Reagents used for the solution studies have been described elsewhere.[3] The following additional reagents for the preparation of the solid complexes were obtained from Aldrich Chemical Co. and used without further purification: 3-iodopyridine, 3,5-lutidine, 2-methylimidazole, and 5,6-dimethylbenzimidazole. Imidazole (Aldrich) was recrystallized as colorless needles from benzene (twice), and benzimidazole (Aldrich) was recrystallized twice from ethanol as a pale yellow powder.

Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn., by Bernhardt Mikroanalytisches Laboratorium, Mülheim, Germany, and by Micro-Tech Laboratories, Skokie, Ill.

Co^{II}(salen).—This complex was prepared by the method of West[9] as lustrous maroon plates in 86–94% yields. *Anal.* Calcd for $CoC_{16}H_{14}N_2O_2$: C, 59.08; H, 4.34; N, 8.62. Found: C, 59.01; H, 4.26; N, 8.82.

Co^{II}(salen)(imidazole).—A solution of Co^{II}(salen) in methylene chloride (0.650 g, 2.0 mmol, in 250 ml) was filtered and treated with a filtered solution of imidazole in the same solvent (0.136 g, 2.0 mmol, in 20 ml). The solution darkened immediately, and a brownish red precipitate formed; the latter was collected after 4 hr, washed with methylene chloride and diethyl ether, and dried *in vacuo* at 78.5° for 7 hr and then at ambient temperature for 3 days; yield, 0.681 g (1.73 mmol, 87%). The complex was stable in air for at least 2 days and was very slightly soluble in acetone and insoluble in methanol, water, and chloroform. *Anal.* Calcd for $Co_{19}H_{18}N_4O_2$: C, 58.02; H, 4.61; N, 14.25. Found: C, 57.96; H, 4.68; N, 14.15.

Co^{II}(salen)(2-methylimidazole).—Methylene chloride solutions of Co^{II}(salen) (0.650 g, 2.0 mmol, in 250 ml) and 2-methylimidazole (1.64 g, 20.0 mmol, in 80 ml, filtered) were mixed. The precipitate which formed immediately was collected by gravity filtration, washed with methylene chloride and then with acetone (yield of iridescent red-gold microcrystalline powder, 0.653 g (80%)), and dried *in vacuo* at 78.5° for 9 hr. *Anal.* Calcd for $CoC_{20}H_{20}N_4O_2$: C, 58.97; H, 4.95; N, 13.76. Found: C, 58.75; H, 4.97; N, 13.76.

Co^{II}(salen)(benzimidazole).—To a filtered solution of Co^{II}(salen) in methylene chloride (0.650 g, 2.0 mmol, in 240 ml) was added a filtered solution of benzimidazole in the same solvent (0.236 g, 2.0 mmol, in 50 ml). The reaction mixture immediately darkened, and a precipitate began to form and continued to separate as the solution was allowed to stand for 2.5 hr and to evaporate to about half the original volume. The fine reddish orange powder was collected, washed with methylene chloride, and dried *in vacuo* at 65° for 3.5 hr and then at ambient temperature for 3 days; yield, 0.475 g (53%). The compound was slightly soluble in methylene chloride and acetone and very slightly soluble in methanol and ethanol. Infrared spectra indicate that the material is stable in air over a period of several hours. *Anal.* Calcd for $CoC_{23}H_{20}N_4O_2$: C, 62.30; H, 4.55; N, 12.64. Found: C, 61.70; H, 4.31; N, 12.54.

Co^{II}(salen)(5,6-dimethylbenzimidazole).—A chloroform solution of Co^{II}(salen) (0.650 g, 2.0 mmol, in 200 ml) was treated with a filtered solution of 5,6-dimethylbenzimidazole in the same solvent (0.292 g, 2.0 mmol, in 50 ml). Evaporation of about half the solvent yielded 0.43 g (45%) of a fine reddish gold powder, which was washed with a small amount of chloroform and dried *in vacuo* at 78.5° for 7 hr. The same product was also obtained from an analogous procedure using methylene chloride as solvent. *Anal.* Calcd for $CoC_{25}H_{24}N_4O_2$: C, 63.69; H, 5.13; N, 11.89. Found: C, 63.23; H, 4.87; N, 12.16.

Co^{II}(salen)(pyridine).—This complex was prepared in 67% yield by the method of Bailes and Calvin[10] and the crude product was recrystallized from pyridine–water as red-orange crystals. *Anal.* Calcd for $CoC_{21}H_{19}N_3O_2$: C, 62.38; H, 4.74; N, 10.39. Found: C, 61.90; H, 4.68; N, 10.21.

Co^{II}(salen)(3,5-lutidine)·H_2O.—A suspension of Co^{II}(salen) in methylene chloride solution (0.33 g, 1.02 mmol, in 30 ml) was treated with an excess (*ca.* 15 ml) of 3,5-lutidine and the reaction solution was filtered and then concentrated until a substantial fraction of material had precipitated. The red-brown powder collected was washed with acetone and then diethyl ether and dried under nitrogen for 16 hr; yield, 0.18 g (40%). The ir spectrum of this compound indicates the presence of water. *Anal.* Calcd for $C_{28}H_{25}N_3O_3$: C, 61.33; H, 5.60; N, 9.33. Found: C, 61.03; H, 4.82; N, 9.16.

Co^{II}(salen)(3-iodopyridine).—The starting complex Co^{II}(salen) was suspended in methylene chloride (0.20 g, 0.62 mmol, in 90 ml) and treated with a small quantity of 3-iodopyridine to effect solution. The remaining 3-iodopyridine was dissolved in methylene chloride (2.0 g total, 9.8 mmol, in 10 ml), and the solution was filtered and added to the complex solution. A flaky gold precipitate formed in the solution as the solvent was allowed to evaporate slowly. The product was washed well with diethyl ether, then dried *in vacuo* at 78.5° for 7 hr; yield, 0.14 g (42%). *Anal.* Calcd for $CoC_{21}H_{18}IN_3O_2$: C, 47.57; H, 3.42; N, 7.93. Found: C, 47.79; H, 3.40; N, 7.79.

Co^{II}(saloph)(imidazole).—The preparation of this complex appears elsewhere.[3]

Results

Methylene Chloride Solution.—The magnetic moment of Co^{II}(salen), measured by the Evans method,[8] was determined as 2.5 BM at 40° in methylene chloride solution. Addition of 1-methylimidazole (0.7 *M;* at this concentration equilibrium 4 lies to the right) increased the magnetic moment to 3.4 BM. For most of the solution measurements, however, Co^{II}(saloph)B complexes were used since for them K_1 (eq 4) was found

---

[7] B. N. Figgis and J. Lewis in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience, New York, N. Y., 1960, p 403.

[8] D. F. Evans, *J. Chem. Soc.*, 2003 (1959). χ_M = (concentration)$^{-1}$·(chemical shift)(7.6 × 10^{-6}) cgs emu.

[9] B. O. West, *ibid.*, 395 (1954).

[10] R. H. Bailes and M. Calvin, *J. Amer. Chem. Soc.*, **69**, 1886 (1947).

to be approximately 50 times greater than that for the analogous salen complexes,[2,3] and thus lower concentrations of added ligand (B) were required. The values obtained with various ligands were as follows: 1-methylimidazole, 3.8 BM; 3,4-lutidine, 3.1 BM; pyridine, 2.9 BM; diphenylphosphine, 2.5 BM; tri-*n*-butylphosphine, 2.7 BM.

The magnetic susceptibilities of the complexes containing 1-methylimidazole, pyridine, and 3,4-lutidine decreased with decreasing temperature, and the magnetic moments approached limiting values of 2.0 ± 0.2 BM.[11] The larger values of both K_1[3] and χ for the 1-methylimidazole complex allowed the most accurate determination of the temperature dependence of χ with the least interference from additional equilibria such as (5), Table I.

TABLE I

TEMPERATURE DEPENDENCE OF THE MAGNETIC SUSCEPTIBILITY OF Co^{II}(saloph)(1-methylimidazole) IN METHYLENE CHLORIDE SOLUTION

Temp, °K	$10^5\chi_M$,[a] cgs emu	Temp, °K	$10^5\chi_M$,[a] cgs emu	Temp, °K	$10^5\chi_M$,[a] cgs emu
293	504	243	507	213	471
273	520	233	498	203	449
253	514	223	487	193	427

[a] Concentration was 0.059 *M* Co^{II}(saloph)(1-methylimidazole); a 0.014 molar excess of 1-methylimidazole was added to drive equilibrium 4 to the right.

Determination of the magnetic susceptibility in solution is much less accurate than in the solid state for the following reasons: (1) temperature cannot be determined so precisely in solution (±3°); (2) volume changes must be taken into account; (3) corrections for an excess of ligand must be applied; and (4) equilibria such as (4) and (5) complicate treatment of the data. For these reasons methods were developed for preparing solid samples of the complexes.

Room-Temperature Measurements.—The magnetic moments measured at room temperature for the compounds prepared in this study are collected in Table II.

TABLE II

ROOM-TEMPERATURE MAGNETIC MOMENTS FOUND FOR Co^{II}(saloph)(imidazole) AND FOR SEVERAL Co^{II}(salen)B COMPLEXES

Complex	μ(22°), BM	Complex	μ(22°), BM
Co(salen)(imidazole)	1.94	Co(salen)(benzimidazole)	2.61
Co(salen)(3-iodopyridine)	2.15	Co(salen)(5,6-dimethylbenzimidazole)	2.75[a]
Co(salen)(pyridine)	2.35[a]	Co(salen)(2-methylimidazole)	3.48
Co(salen)(3,5-lutidine)·H_2O	2.55	Co(saloph)(imidazole)	3.40

[a] Measured at 21°.

Magnetic susceptibilities were independent of the applied field. Some complexes were prepared several times and the moments determined for the different samples were in excellent agreement (<±0.05 BM). With the exception of the air-sensitive and hygroscopic 3,5-lutidine complex, the susceptibility of the complexes did not change when the solid samples were exposed to air.

Temperature-Dependence Studies.—None of the complexes exhibited Curie–Weiss behavior over the temperature ranges investigated (Table III). Since the room-temperature magnetic moments of most of the complexes were close to that expected for low-spin complexes, the effect on the susceptibility of increasing the temperature was of greatest interest. Although the existing apparatus was designed specifically for temperatures between liquid nitrogen and *ca.* 60°, design changes made possible measurements as high as 140°, with some risk to equipment. As a result of these limitations, only the Co^{II}(salen)(5,6-dimethylbenzimidazole) complex was studied over the entire accessible temperature range. This particular complex was chosen for several reasons: (1) the obvious biological importance of the axial ligands, (2) the large room-temperature moment near the middle of the observed range of values, making it representative, and (3) the thermal stability of the complex.

The data obtained are presented in Table III and Figure 1. It should be noted that the measured susceptibilities were independent of the history of the

TABLE III

DEPENDENCE OF MAGNETIC SUSCEPTIBILITY ON TEMPERATURE FOR SEVERAL Co^{II}(salen)B COMPLEXES

Temp, °K	$10^6\chi_M$, cgs emu	Temp, °K	$10^6\chi_M$, cgs emu
A. Co(salen)(2-methylimidazole)			
196	3824	295	5094
B. Co(salen)(imidazole)			
295	1584	413	2183
363	1844		
C. Co(salen)(5,6-dimethylbenzimidazole)			
81	5706	337	3678
168	2917	356	3744
199	2714	370	3880
225	2657	397	4035
293	3185	415	4082
306	3388		

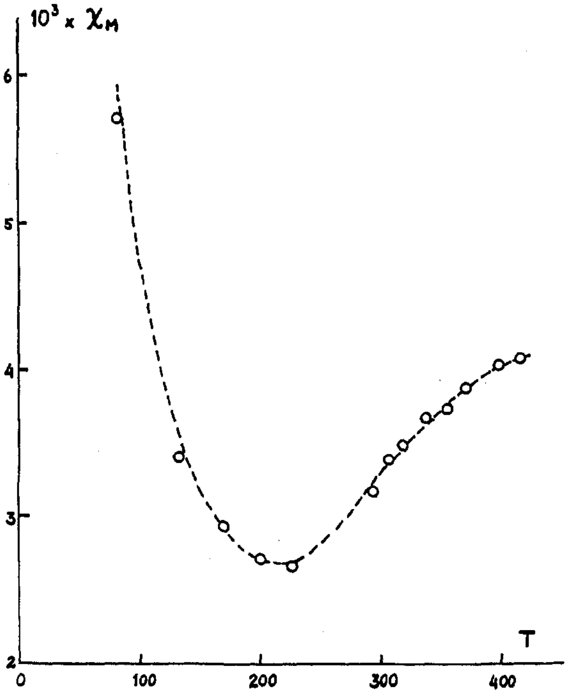


Figure 1.—Plot of χ_M (cgs emu) *vs.* *T* for Co(salen)(5,6-dimethylbenzimidazole).

---

[11] There were concomitant changes in the absorption spectra of these solutions consistent with the formation of greater percentages of low-spin complexes on cooling. Evidence supporting a five-coordinate species has been presented.[2,3]

sample and that after both heating and cooling the measured susceptibility coincided with the initial room-temperature value. Furthermore, the infrared spectrum of the sample subjected to the temperature-variation studies was identical in every detail with that of the starting material. Another sample, studied over a more limited temperature range, gave the same results within experimental error.

Discussion

The close correspondence between the magnetic properties of these complexes in solution and as solids suggests that in both instances five-coordinate complexes are involved.[11] Although a structural determination has not been carried out for this type of complex, square-pyramidal geometry is assumed since the salen and saloph ligands generally adopt a planar configuration.[12-14] If the axial ligand is assumed to be planar and normal to the in-plane ligand, these complexes have C_s symmetry, and the equilibrium between high- (HS) and low-spin (LS) forms can be represented as $^4A'' \rightleftharpoons {}^2A'$.

The anomalous dependence of the magnetic susceptibility on temperature observed in this study closely parallels that exhibited by other complexes which are believed to exist in a state of dynamic spin equilibrium.[15-18] Furthermore, Co^{II}(salen)(5,6-dimethylbenzimidazole) (an N_3O_2 donor atom set) was found to exhibit a remarkably similar temperature dependence to that reported for *N,N'*-bis(3-ethoxysalicylidene)ethylenediaminocobalt(II) monohydrate[17] (an N_2O_3 donor set). For this latter complex a simple spin equilibrium between a ^4T (4.5 BM) and ^2E (2.0 BM) was used to treat the data quantitatively, and a plot of ln K *vs.* T^{-1} gave a straight line (K = [LS]/[HS]), ΔH = -3 kcal mol^{-1}.[17] This type of treatment was first applied to cobalt(II) octahedral complexes by Stoufer, Busch, and Hadley.[15] Although such a simple model should not adequately describe the anomalous temperature dependence,[15,17,18] the method has proved successful for several types of complexes. The development of more meaningful approaches is the subject of much current research.[18]

In the above studies and in that reported here it was not possible to increase the temperature sufficiently to effect exclusive formation of the high-spin species (>95%). However, the related high-spin complex *N,N'*-bis(3-methoxysalicylidene)ethylenediaminocobalt(II) monohydrate exhibits a moment of 4.6 BM at 360°K.[17] An authenticated example of a square-pyramidal cobalt(II) complex, bis(*N*-(5-chlorosalicylidene)-*N',N'*-diethylethylenediamino)cobalt(II), has a moment between 4.1 and 4.7 BM.[19] Barefield, Busch, and Nelson[16] placed the expected value for high-spin square-pyramidal cobalt(II) between 4.2 and 4.6 BM. Treatment of the data obtained for Co^{II}(salen)(5,6-dimethylbenzimidazole) using values less than 4.5 BM results in distinct curvature. If the limiting values 4.6 and 2.0 BM are applied and Curie behavior is assumed for each spin form, a good linear plot of log K *vs.* T^{-1} (Figure 2) is obtained, from which ΔH is calculated[20] as -3.2 ± 0.5 kcal mol^{-1}. An analogous treatment of the less precise data from the solution measurements for Co^{II}(saloph)(1-methylimidazole) results in a reasonably straight line from which ΔH is calculated as -1.7 ± 0.5 kcal mol^{-1} when limiting values of 4.6 and 1.8 BM are utilized.

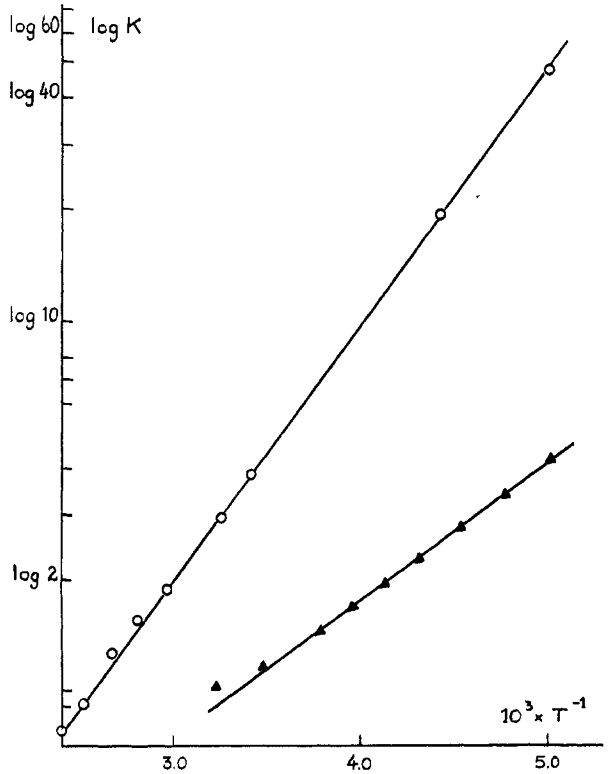


Figure 2.—Plot of log $K(HS \rightleftharpoons LS)$ *vs.* T^{-1} for (○) Co^{II}(salen)-(5,6-dimethylbenzimidazole) (solid state) and (▲) Co^{II}(saloph)-(1-methylimidazole) in methylene chloride solution.

Co(II)–salen complexes containing pyridine[17] and substituted pyridines were found to have similar moments close to the expected low-spin value (Table II). By contrast, the moments of complexes with imidazole and substituted imidazoles varied from 1.94 to 3.48 BM and were generally higher than those of the pyridine complexes with a given Schiff's base. This difference may be related to the reason that imidazole and substituted imidazoles are so effective in promoting electron-transfer reactions.[2] Addition of a second ligand B may be more favorable if the five-coordinate complex is already of the high-spin form.[21,22]

---

(12) D. Hall and H. Moore, *Proc. Chem. Soc., London*, 256 (1960).

(13) F. J. Llewellyn and T. N. Waters, *J. Chem. Soc.*, 2639 (1960).

(14) D. Hall and T. N. Waters, *ibid.*, 2644 (1960).

(15) R. C. Stoufer, D. H. Busch, and W. B. Hadley, *J. Amer. Chem. Soc.*, **83**, 3732 (1961).

(16) E. K. Barefield, D. H. Busch, and S. M. Nelson, *Quart. Rev., Chem. Soc.*, **22**, 457 (1968).

(17) A. Earnshaw, P. C. Hewlett, E. A. King, and L. F. Larkworthy, *J. Chem. Soc. A*, 241 (1968).

(18) R. L. Martin and A. H. White, *Transition Metal Chem.*, **4**, 113 (1968).

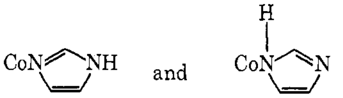
(19) L. Sacconi, M. Ciampolini, and G. P. Speroni, *Inorg. Chem.*, **4**, 1116 (1965).

(20) The magnitude of ΔS is dependent on the value of μ_{HS} used in the calculations. However, ΔH is not so dependent on μ_{HS} for values in the range for which a linear plot is obtained.

(21) We are aware of the errors which arise from attempting to describe the behavior of complexes in solution with reference to the solid-state properties but feel that the correspondence between solid-state and solution magnetic data justifies this argument. See footnote 22.

(22) For this reason as well as those given in ref 20, the solution studies, although less accurate, are described briefly in this paper. It seems likely that the form of Co^{II}(salen)(imidazole) isolated may in fact be the less stable of the two square-pyramidal isomers since it is extremely insoluble in methylene chloride. In any case, this complex was so insoluble as to preclude any kinetic measurements, and it is not certain that it would undergo electron-transfer reactions. On the other hand, Co^{II}(salen)(pyridine), which favors halogen abstraction, and Co^{II}(saloph)(imidazole), which favors electron transfer, are both quite soluble in methylene chloride.

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



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).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF ALBERTA, EDMONTON, ALBERTA, CANADA

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

BY D. J. FRANCIS AND R. B. JORDAN*

Received June 11, 1971

The acid-catalyzed hydrolysis of the $(phen)_2CoCO_3^+$ and $(bipy)_2CoCO_3^+$ ions was found to follow the rate law $-d \ln [complex]/dt = k_0 + k_1[H^+]$ 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

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

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

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

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

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 tet*b* 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 $(phen)_2$-

---

(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).