1738 Inorganic Chemistry, Vol. 9, No. 7, 1970

Contribution from the Department of Chemistry,
University of Nebraska, Lincoln, Nebraska 68508

Cobalt(II) Chloride–Pyridine Equilibria and the Exchange of Pyridine with Dichlorotetrakis(pyridine)cobalt(II) Investigated by Nitrogen-14 Nuclear Magnetic Resonance

By G. D. Howard and R. S. Marianelli[1]

Received July 8, 1969

The equilibrium constant, $[CoPy_2Cl_2][Py]^2/[CoPy_4Cl_2]$, was determined from ^{14}N chemical shift data to be $2.3 \pm 1.2\ M^2$ at 38°, with ΔH and ΔS for the equilibrium being 13.0 ± 0.9 kcal/mol and 43.4 ± 2.2 eu, respectively. The mean lifetime of pyridine on $CoPy_4Cl_2$ was determined from ^{14}N nuclear magnetic resonance data to be $(1.5 \pm 0.2) \times 10^{-7}$ sec at 25°, with $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the exchange being 13.2 ± 0.5 kcal/mol and 17 ± 2 eu, respectively. T_{1e} for $CoPy_4Cl_2$ was estimated to be 8×10^{-13} sec.

Introduction

The system

$$CoPy_4Cl_2 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} CoPy_2Cl_2 + 2Py \qquad (1)$$

has been studied for many years[2–8] and is of current interest.[9] The equilibrium constant K_1 in pyridine, $[CoPy_2Cl_2][Py]^2/[CoPy_4Cl_2]$, which is significantly different from K_1 in other solvents, until now has only been approximated.[2] A more accurate evaluation of K_1, which is reported in this study, is of interest for kinetic studies on this system.

The equilibrium exchange rate for the tetrahedral species

$$CoPy_3Cl_2 \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} CoPy_2Cl_2 + Py \qquad (2)$$

and its activation parameters have been reported.[9] To understand equilibrium 1 more fully, it is also necessary to know the exchange rate constants and their activation parameters for the equilibrium

$$CoPy_4Cl_2 \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} CoPy_3Cl_2 + Py \qquad (3)$$

The ^{14}N nmr data reported in this study determined some of the kinetic parameters for equilibrium 3.

Experimental Section

The cobalt metal used in the preparations was 99.999% pure from Spex Industries. Cobalt concentrations were determined by EDTA titrations using murexide indicator.[10] Reagent grade pyridine was further purified by distillation. All other reagents were reagent grade purity.

$CoCl_2 \cdot xH_2O$ was prepared by allowing cobalt metal to react with hydrochloric acid. $CoPy_2Cl_2$ was prepared from the $CoCl_2 \cdot xH_2O$ by the method of Gill, *et al.*[4] Since this is a well-characterized preparation only the per cent cobalt was determined. *Anal.* Calcd for $CoPy_2Cl_2$: Co, 20.5. Found: Co, 20.6.

The solutions of $CoPy_2Cl_2$ in pyridine were prepared and the nmr sample tubes were sealed under vacuum without exposure to the atmosphere or moisture by using standard vacuum-line techniques. The pyridine was stirred over Linde 3A molecular sieves. A portion of the pyridine was transferred to a second flask containing the dry solid $CoPy_2Cl_2$ complex. This solution was stirred and the pyridine was transferred back to the flask containing the molecular sieves. The solid purple complex was heated until the blue tetrahedral complex formed. The pyridine was again stirred with the molecular sieves, and then a small portion was transferred a second time to the flask containing the solid complex. A portion of the resulting pink solution was transferred to a 9-mm o.d. nmr sample tube, and the tube was sealed.

A standard broad-line nmr spectrometer equipped with a Varian variable-temperature unit was used. The broad-line transmitter and receiver were designed and built by Torgeson.[11] A copper–constantan thermocouple placed in the temperature well of the sealed nmr tube was used to monitor the temperature. The spectrometer was operated at a radiofrequency of 4.334 MHz.

The magnetic field strengths at which resonances occur for various samples are proportional to the field offset on the slow-sweep unit. By measuring the voltage at which the resonances occur and by calibrating the slow-sweep unit in terms of gauss per millivolt it is possible to determine the ^{14}N chemical shifts of the Co(II) samples and pure pyridine relative to the pure acetonitrile ^{14}N resonance. The signals were detected in the derivative of absorption mode with the modulation amplitude adjusted to give the best possible signal to noise ratio.[12,13]

Values of three of the chemical shifts were determined by an alternate method. Absorption mode signals from the probe were detected with the audio reference phase angle set at 90° and the modulation frequency larger than the line width. The modulation amplitude was adjusted so that there were appreciable signals from the center band and the first and second side bands.[12,13] The first and second low-field side-band signals of the sample were recorded; then the sample was replaced in the probe with a pure pyridine sample while the slow-sweep unit continued its sweep. The center band and the first and second high-field side-band signals of the pyridine sample were recorded. Measurements and calibrations in radians per second of the distances between the signals gave a direct determination of the ^{14}N chemical shifts of the Co(II) solutions relative to the ^{14}N resonance of pyridine. The results obtained in this manner were less precise

---

(1) To whom correspondence and reprint requests should be addressed.

(2) L. I. Katzin, *J. Chem. Phys.*, **35**, 467 (1961).

(3) H. C. A. King, E. Koros, and S. M. Nelson, *J. Chem. Soc.*, 5449 (1963).

(4) N. S. Gill, R. S. Nyholm, G. A. Barclay, T. I. Christie, and P. J. Pauling, *J. Inorg. Nucl. Chem.*, **18**, 88 (1961).

(5) J. D. Dunitz, *Acta Cryst.*, **10**, 307 (1957).

(6) W. Libus and I. Uruska, *Inorg. Chem.*, **5**, 256 (1966).

(7) R. L. Carlin, *Transition Metal Chem.*, **1**, 1 (1965).

(8) L. I. Katzin, *ibid.*, **3**, 56 (1966).

(9) R. D. Farina and J. H. Swinehart, *J. Am. Chem. Soc.*, **91**, 568 (1969).

(10) F. J. Welcher, "The Analytical Uses of Ethylenediaminetetraacetic Acid," D. Van Nostrand Co., Inc., Princeton, N. J., 1958, p 230.

(11) D. R. Torgeson, *Rev. Sci. Instr.*, **38**, 612 (1967).

(12) J. H. Burgess and R. M. Brown, *ibid.*, **23**, 334 (1952), and references therein.

(13) J. V. Acrivos, *J. Chem. Phys.*, **36**, 1097 (1962).

than those obtained by the first method but agreed well with them. The ^{14}N resonances of pyridine for the Co(II) solutions were shifted to lower magnetic fields relative to the ^{14}N resonance of pure pyridine, treated in this paper as a negative chemical shift.

The observed chemical shifts were not corrected for changes in the bulk magnetic susceptibilities of the samples. It was estimated that these corrections would change the results less than 1%.

The line widths of the signals of the samples were determined from the full line widths at half-height of the absorption signals recorded while using modulation frequencies larger than the line widths, an audio reference phase angle of 0°, and the modulation amplitude adjusted to give maximum first side-band signals.[12,13] All of the line widths were determined under conditions of slow passage and negligible saturation. Most of the line widths reported are the average of 20 determinations.

All straight-line plots were done by a WATFOR least-squares computer program.[14] The program calculated the standard deviations. One standard deviation is used as the limit of experimental error for all values reported, except K_1.

Results

General Theory.—For this system it has been shown that the only species present are $\mathrm{CoPy_2Cl_2}$ ($\mathrm{T_d}$), $\mathrm{CoPy_3Cl_2}$ (I), and *trans*-$\mathrm{CoPy_4Cl_2}$ ($\mathrm{O_h}$).[2,3,9] Swift and Connick[15] have shown that for a dilute solution of paramagnetic species with no direct exchange of solvent molecules between the paramagnetic species, which is assumed true for this system, the total observed chemical shift, $\Delta\omega_o$, can be expressed as

$$\begin{aligned} -\Delta\omega_o = {} & P_{\mathrm{T_d}}\Delta\omega_{\mathrm{T_d}}/\tau_{\mathrm{T_d}}^2[(1/T_{2\mathrm{T_d}} + 1/\tau_{\mathrm{T_d}})^2 + \Delta\omega_{\mathrm{T_d}}^2] + \\ & P_{\mathrm{I}}\Delta\omega_{\mathrm{I}}/\tau_{\mathrm{I}}^2[(1/T_{2\mathrm{I}} + 1/\tau_{\mathrm{I}})^2 + \Delta\omega_{\mathrm{I}}^2] + \\ & P_{\mathrm{O_h}}\Delta\omega_{\mathrm{O_h}}/\tau_{\mathrm{O_h}}^2[(1/T_{2\mathrm{O_h}} + 1/\tau_{\mathrm{O_h}})^2 + \Delta\omega_{\mathrm{O_h}}^2] \end{aligned} \quad (4)$$

where P is the probability of a pyridine molecule being in the first coordination sphere of the species, $\Delta\omega$ is the difference in radians per second between the ^{14}N resonance of a pyridine molecule in the bulk solvent and the ^{14}N resonance of a pyridine molecule in the first coordination sphere of the species, $1/T_2$ is the transverse relaxation rate of a pyridine molecule in the first coordination sphere of the species, τ is the mean lifetime of a pyridine molecule in the first coordination sphere of the species, and the subscripts $\mathrm{T_d}$, I, and $\mathrm{O_h}$ indicate the species that the parameters pertain to. $\mathrm{CoPy_2Cl_2}$ can exchange pyridine by three routes: a dissociative path leading to the intermediate $\mathrm{CoPyCl_2}$, an associative path leading to the intermediate $\mathrm{CoPy_3Cl_2}$, and a concerted path. $\mathrm{CoPy_2Cl_2}$ does not significantly dissociate to $\mathrm{CoPyCl_2}$.[2,3,9] This pathway would have associated with it a long $\tau_{\mathrm{T_d}}$, thus making the term $P_{\mathrm{T_d}}\Delta\omega_{\mathrm{T_d}}/\tau_{\mathrm{T_d}}^2[(1/T_{2\mathrm{T_d}} + 1/\tau_{\mathrm{T_d}})^2 + \Delta\omega_{\mathrm{T_d}}^2]$ very small. For the second possibility one need only consider the $\mathrm{CoPy_3Cl_2}$ intermediate, which has been postulated to exist in trace amounts.[9] Since P_{I} would be very small, the term $P_{\mathrm{I}}\Delta\omega_{\mathrm{I}}/\tau_{\mathrm{I}}^2[(1/T_{2\mathrm{I}} + 1/\tau_{\mathrm{I}})^2 + \Delta\omega_{\mathrm{I}}^2]$ does not contribute significantly to $\Delta\omega_o$.

Although our experimental results can be explained without considering a concerted exchange, this type of mechanism cannot be definitely ruled out solely on the basis of our data.[16] However, our data would put rather severe restrictions on the rate constant and activation parameters for such a mechanism for exchange. Also, it seems unlikely that both the associative and concerted pathways would be operative simultaneously.

Because of these considerations it is possible to simplify eq 4 to

$$-\Delta\omega_o = P_{\mathrm{O_h}}\Delta\omega_{\mathrm{O_h}}/\tau_{\mathrm{O_h}}^2[(1/T_{2\mathrm{O_h}} + 1/\tau_{\mathrm{O_h}})^2 + \Delta\omega_{\mathrm{O_h}}^2] \quad (5)$$

At $10^3/T < 4.2$, $1/\tau_{\mathrm{O_h}}$, $\Delta\omega_{\mathrm{O_h}} \gg 1/T_{2\mathrm{O_h}}$ as will be shown later in this paper. Therefore eq 5 can be simplified to

$$-\Delta\omega_o = P_{\mathrm{O_h}}\Delta\omega_{\mathrm{O_h}}/[1 + (\tau_{\mathrm{O_h}}\Delta\omega_{\mathrm{O_h}})^2] \quad (6)$$

The line broadening can be related to the exchange rate by[15]

$$\begin{aligned} \pi\Delta\nu = 1/T_{2\mathrm{P}} = {} & (P_{\mathrm{T_d}}/\tau_{\mathrm{T_d}})(1/T_{2\mathrm{T_d}}^2 + 1/T_{2\mathrm{T_d}}\tau_{\mathrm{T_d}} + \\ & \Delta\omega_{\mathrm{T_d}}^2)/[(1/T_{2\mathrm{T_d}} + 1/\tau_{\mathrm{T_d}})^2 + \Delta\omega_{\mathrm{T_d}}^2] + (P_{\mathrm{I}}/\tau_{\mathrm{I}})(1/T_{2\mathrm{I}}^2 + \\ & 1/T_{2\mathrm{I}}\tau_{\mathrm{I}} + \Delta\omega_{\mathrm{I}}^2)/[(1/T_{2\mathrm{I}} + 1/\tau_{\mathrm{I}})^2 + \Delta\omega_{\mathrm{I}}^2] + \\ & (P_{\mathrm{O_h}}/\tau_{\mathrm{O_h}})(1/T_{2\mathrm{O_h}}^2 + 1/T_{2\mathrm{O_h}}\tau_{\mathrm{O_h}} + \Delta\omega_{\mathrm{O_h}}^2)/[(1/T_{2\mathrm{O_h}} + \\ & 1/\tau_{\mathrm{O_h}})^2 + \Delta\omega_{\mathrm{O_h}}^2] \end{aligned} \quad (7)$$

where $\Delta\nu$ is the difference in hertz between the full line width at half-height of the sample signal and the full line width at half-height of the pure pyridine signal at the same temperature. Because of the same considerations that apply to $\Delta\omega_o$, the $\mathrm{T_d}$ and I terms can be neglected, and for $10^3/T < 4.2$, $1/\tau_{\mathrm{O_h}}$, $\Delta\omega_{\mathrm{O_h}} \gg 1/T_{2\mathrm{O_h}}$, simplifying eq 7 to

$$1/T_{2\mathrm{P}} = [(P_{\mathrm{O_h}}/T_{2\mathrm{O_h}}) + P_{\mathrm{O_h}}\tau_{\mathrm{O_h}}\Delta\omega_{\mathrm{O_h}}^2]/[1 + (\tau_{\mathrm{O_h}}\Delta\omega_{\mathrm{O_h}})^2] \quad (8)$$

$\Delta\omega_{\mathrm{O_h}}$ can be related to the scalar coupling constant, A, by the equation[17]

$$\Delta\omega_{\mathrm{O_h}}/\omega_o = S(S + 1)\gamma_e A/3kT\gamma_{^{14}\mathrm{N}} \quad (9)$$

where ω_o is the Larmor frequency for ^{14}N in radians per second, γ_e is the electronic magnetogyric ratio, and $\gamma_{^{14}\mathrm{N}}$ is the magnetogyric ratio of ^{14}N. $1/T_{2\mathrm{O_h}}$ is given by the sum of a dipolar term, DD, and a scalar coupling term, SC.[18-20] If the correlation times for the DD and

$$1/T_{2\mathrm{O_h}} = \mathrm{DD} + \mathrm{SC} \quad (10)$$

SC terms are assumed to be equal to the longitudinal and transverse electron spin relaxation times, T_{1e} and T_{2e}, respectively, with $T_{1e} = T_{2e}$ and $T_{1e}^2\omega_e^2 \ll 1$, where ω_e is the Larmor frequency for an electron, then DD and SC are given by[18-20]

$$\mathrm{DD} = 4\mu_{\mathrm{eff}}^2\beta^2\gamma_{\mathrm{N}^{14}}^2 T_{1e}/3r^6 \quad (11)$$

$$\mathrm{SC} = 2S(S + 1)A^2T_{1e}/3\hbar^2 \quad (12)$$

where μ_{eff} is the magnetic moment of the complex, β is

---

[14] The authors are grateful to William Purcell for the use of his program.

[15] T. J. Swift and R. E. Connick, *J. Chem. Phys.*, **37**, 307 (1962).

[16] Preliminary work with $\mathrm{NiPy_4Cl_2}$, $\mathrm{CoPy_4Br_2}$, and $\mathrm{CoPy_4(SCN)_2}$ is also consistent with the explanation offered for the $\mathrm{CoPy_4Cl_2}$ system.

[17] N. Bloembergen, *J. Chem. Phys.*, **27**, 595 (1957).

[18] I. Solomon, *Phys. Rev.*, **99**, 559 (1955).

[19] I. Solomon and N. Bloembergen, *J. Chem. Phys.*, **25**, 261 (1956).

[20] N. Bloembergen, *ibid.*, **27**, 572 (1957).

the Bohr magnetron, and r is the distance between the nucleus and the electron.

Equilibrium Data.—If the concentration of the octahedral cobalt complex, $[\mathrm{Co_{O_h}}^{2+}]$, is considered as being equal to the analytical concentration of Co(II), $C_{\mathrm{Co(II)}}$, the values for Figure 1 are obtained. Since eq 9 shows that $\Delta\omega_{\mathrm{O_h}}$ is proportional to $1/T$, according to eq 6 if $[\mathrm{Co_{O_h}}^{2+}] = C_{\mathrm{Co(II)}}$, then $T\Delta\omega_o/C_{\mathrm{Co(II)}}$ should approach a maximum value. Instead, $-T\Delta\omega_o/C_{\mathrm{Co(II)}}$ reaches a maximum value and then decreases. This decrease reflects a decrease in the $\mathrm{Co_{O_h}}^{2+}$ concentration, assumed to be due to the shifting to the right of equilibrium 1 with increasing temperature, as reported previously.[2,3,6,9] From eq 6 the concentration of $\mathrm{Co_{O_h}}^{2+}$ can be expressed

$$[\mathrm{Co_{O_h}}^{2+}] = -(\Delta\omega_o/\Delta\omega_{\mathrm{O_h}})[1 + (\tau_{\mathrm{O_h}}\Delta\omega_{\mathrm{O_h}})^2]([\mathrm{Py}]/4) \qquad (13)$$

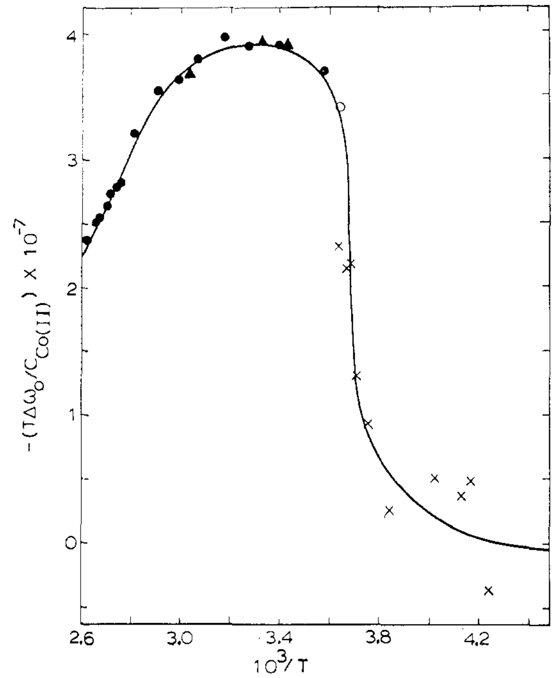

Figure 1.—Temperature dependence of the observed chemical shift in radians per second times the absolute temperature normalized to a 1 M analytical concentration of Co(II). Analytical concentrations of Co(II): closed circles and triangles, $1.48 \times 10^{-2}\,M$; open circle, $9.28 \times 10^{-3}\,M$; X's, $3.51 \times 10^{-3}\,M$. The triangles refer to data obtained by the second method (see Experimental Section). The solid line is drawn to fit the data.

At $10^3/T < 3.0$, $1/\tau_{\mathrm{O_h}} \gg \Delta\omega_{\mathrm{O_h}}$. Therefore, in this temperature region eq 13 can be simplified to

$$[\mathrm{Co_{O_h}}^{2+}] = \frac{\Delta\omega_o[\mathrm{Py}]}{4\Delta\omega_{\mathrm{O_h}}} \qquad (14)$$

If the maximum value of $-T\Delta\omega_o/[\mathrm{Co_{O_h}}^{2+}]$ is assumed to be 3.9×10^7, $T\Delta\omega_{\mathrm{O_h}}$ is equal to 1.2×10^8. From this value and eq 14 the values of $[\mathrm{Co_{O_h}}^{2+}]$ and K_1 in Table I were calculated. At 38° K_1 was determined to be $2.3 \pm 1.3\ M^2$.[21] A plot of ln K_1 *vs.* $10^3/T$, Figure 2, gives a straight line as predicted by

$$\ln K_1 = -\Delta H/RT + \Delta S/R \qquad (15)$$

ΔH and ΔS were calculated from eq 15 to be 13.0 ± 0.9 kcal/mol and 43.4 ± 2.2 eu, respectively. In Figure 3, the values of $-T\Delta\omega_o/[\mathrm{Co_{O_h}}^{2+}]$ are compared to the theoretical values calculated from eq 6 for the $\tau_{\mathrm{O_h}}$ values reported later in this paper.

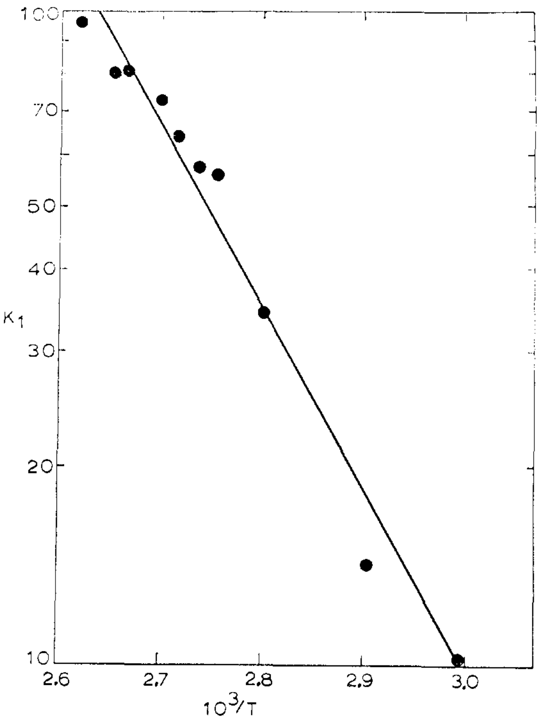

Figure 2.—Temperature dependence of the equilibrium constant, K_1, in M^2. The solid line is a least-squares plot for the data. $C_{\mathrm{Co(II)}} = 1.48 \times 10^{-2}\,M$.

TABLE I

^{14}N CHEMICAL SHIFT DATA FOR $\mathrm{CoPy_4Cl_2}$ AND EQUILIBRIUM CONSTANTS $[\mathrm{CoPy_2Cl_2}][\mathrm{Py}]^2/[\mathrm{CoPy_4Cl_2}]$[a]

$10^3/T$	$-\Delta\omega_o$, radians/sec	$10^2[\mathrm{Co_{O_h}}^{2+}]$, M	K_1, M^2
2.992	1621	1.40	10.1
2.901	1533	1.36	14.2
2.807	1338	1.22	34.5
2.755	1162	1.08	56.7
2.738	1144	1.07	58.9
2.717	1106	1.04	64.3
2.699	1056	1.00	73.4
2.666	1005	0.97	81.0
2.655	1005	0.97	81.0
2.619	930	0.91	96.1

[a] $C_{\mathrm{Co^{2+}}} = 1.48 \times 10^{-2}\,M$.

Kinetic Measurements.—The results obtained are summarized in Table II and Figures 4 and 5. The low solubility of the complex in pyridine and the broad natural line width of pure pyridine lower the precision of the results. At $10^3/T$ values greater than 4.0, $1/T_{2\mathrm{P}}$ is too small to measure accurately.

There was a linear dependence between the total line width of a solution and the $\mathrm{CoPy_4Cl_2}$ concentration. Therefore, the $\mathrm{CoPy_4Cl_2}$ concentration could be varied

---

[21] This limit of error is larger than the standard deviation of the data. It is based on the maximum value of $T\Delta\omega_o/[\mathrm{Co_{O_h}}^{2+}]$ being more than 3.8×10^7 and less than 4.0×10^7.

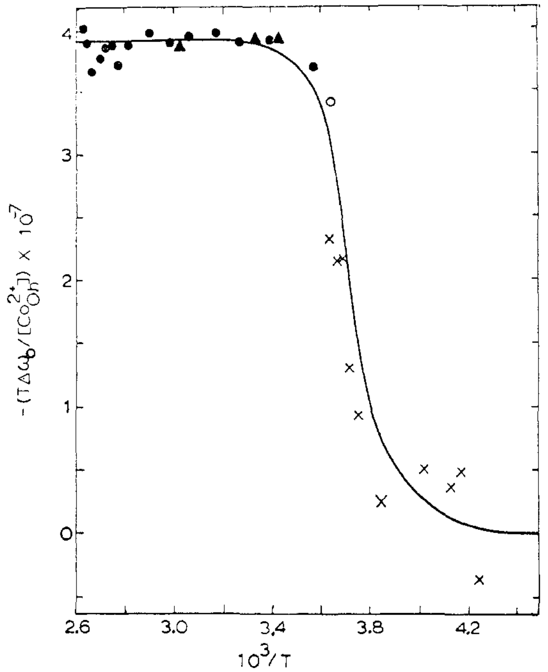

Figure 3.—Temperature dependence of the observed chemical shift in radians per second times the absolute temperature normalized to 1 *M* $CoPy_4Cl_2$ based on K_1 reported in this work. Analytical concentrations of Co(II): closed circles and triangles, 1.48×10^{-2} *M*; open circle, 9.28×10^{-3} *M*; X's, 3.51×10^{-3} *M*. The triangles refer to data obtained by the second method (see Experimental Section). The solid line is calculated from eq 6 for the τ_{O_h} and K_1 values reported in this work.

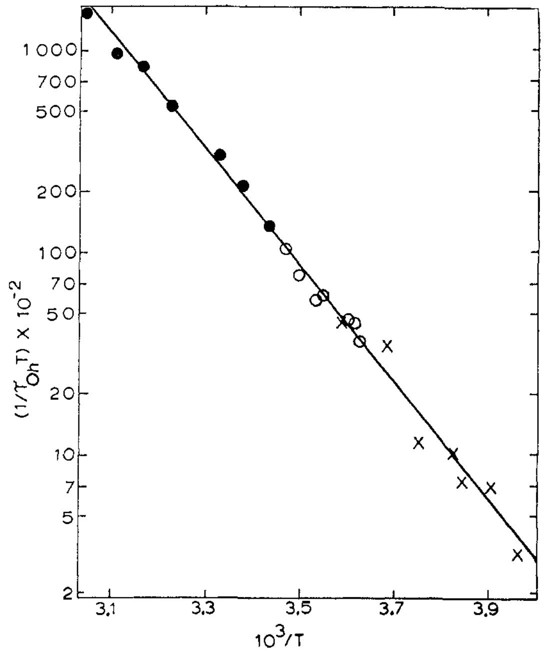

Figure 4.—Temperature dependence of $1/\tau_{O_h}$ in sec^{-1} divided by the absolute temperature. Analytical concentrations of Co(II): closed circles, 1.48×10^{-2} *M*; open circles, 9.28×10^{-3} *M*; X's, 3.51×10^{-3} *M*. The solid line is a least-squares plot for the data.

to give the maximum value of $1/T_{2P}$ at each temperature studied, Figure 5. The $1/T_{2P}$ values shown in Figure 5 were normalized to a 1 *M* analytical concentration of Co(II).

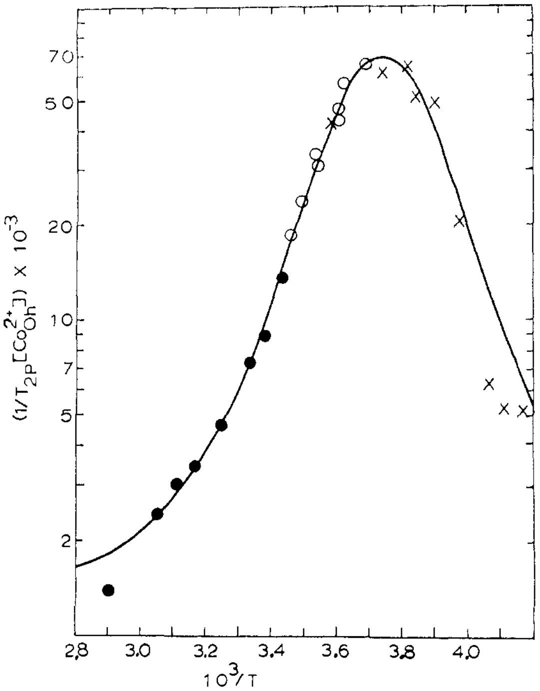

Figure 5.—Temperature dependence of the line broadening in radians per second normalized to 1 *M* $CoPy_4Cl_2$. Concentrations of $CoPy_4Cl_2$: closed circles, 1.48×10^{-2} *M*; open circles, 9.28×10^{-3} *M*; X's, 3.51×10^{-3} *M*. The solid line is calculated from eq 8 for ω_{O_h}, τ_{O_h}, and $1/T_{2O_h}$ values reported in this work.

TABLE II

^{14}N LINE-BROADENING DATA

$10^3/T$, deg^{-1}	ν_{O_h}, Hz	ν_{Py}, Hz	$10^3[Co_{O_h}^{2+}]$, *M*	$1/T_{2P}$, sec^{-1}
2.900	147	141	13.3	19
3.044	175	164	14.2	35
3.105	189	175	14.5	44
3.167	202	186	14.6	50
3.246	224	202	14.7	69
3.333	256	221	14.8	110
3.381	275	227	14.8	151
3.431	304	240	14.8	201
3.461	304	249	9.28	173
3.498	332	260	9.28	226
3.531	369	270	9.28	311
3.546	369	275	9.28	295
3.587	338	290	3.51	150
3.606	430	296	9.28	421
3.617	427	300	9.28	399
3.623	459	303	9.28	490
3.685	402	328	3.51	233
3.745	426	356	3.51	220
3.827	475	402	3.51	229
3.845	470	412	3.51	182
3.905	503	447	3.51	176
3.971	512	484	3.51	88

From Figure 5 it can be seen that at $10^3/T \approx 3.75$, $1/T_{2P}$ reaches its maximum value. The temperature region where $10^3T < 3.75$ corresponds to $1/\tau_{O_h} > 1/T_{2O_h}$, $\Delta\omega_{O_h}$, and $1/T_{2P}$ is given approximately by

$$1/T_{2P} \approx P_{O_h}/T_{2O_h} + P_{O_h}\tau_{O_h}\Delta\omega_{O_h}^2 \qquad (16)$$

From eq 9 and the chemical shift data a value of $A/h = 8.1 \times 10^6$ Hz is calculated. Using this value and eq 12 the SC contribution to $1/T_{2O_h}$ is estimated to be $6 \times 10^{15}T_{1e}$. Using r = 2.2 Å[5] and μ_{eff} = 5.15 BM[4] the

DD contribution to $1/T_{2\mathrm{O_h}}$ is estimated to be $0.1 \times 10^{15} T_{1e}$ from eq 11. The DD term can, therefore, be neglected relative to the SC term. From eq 9 and 12 it can be shown that only when the ratio $\tau_{\mathrm{O_h}}/T_{1e} < 10^5$ is the $P_{\mathrm{O_h}}/T_{2\mathrm{O_h}}$ term important relative to the $P_{\mathrm{O_h}}\tau_{\mathrm{O_h}}\cdot\Delta\omega_{\mathrm{O_h}}^2$ term in eq 16. This occurs where $10^3/T < 3.4$, Figures 4 and 5. The $1/T_{2\mathrm{O_h}}$ term contributes significantly to $1/T_{2\mathrm{P}}$ at $10^3/T < 3.4$ because it is relatively temperature independent, while the $\tau_{\mathrm{O_h}}\Delta\omega_{\mathrm{O_h}}^2$ term decreases rapidly with increasing temperature. On this basis the line-width data were treated in the following manner.

The line-width data for $10^3/T > 3.4$ were used with the chemical shift data to calculate the $\tau_{\mathrm{O_h}}$ values using eq 8, neglecting the $P_{\mathrm{O_h}}/T_{2\mathrm{O_h}}$ term. From the expression

$$1/\tau_{\mathrm{O_h}} = (kT/h)e^{-\Delta H^{\ddagger}/RT}e^{\Delta S^{\ddagger}/R} \qquad (17)$$

$\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were determined to be 13.2 ± 0.5 kcal/mol and 17 ± 2 eu, respectively, Figure 4.

From the extrapolated $\tau_{\mathrm{O_h}}$ values, the chemical shift data, the line-width data for $10^3/T < 3.4$, and eq 8, $1/T_{2\mathrm{O_h}}$ was estimated to be 5×10^3 sec^{-1}. Applying this value to eq 12 gave an estimated T_{1e} of 8×10^{-13} sec. The determined T_{1e} values exhibited little temperature dependence, but the values of T_{1e} obtained were too scattered to allow a precise determination of its temperature dependence. This estimate of T_{1e} seems quite reasonable for an octahedral Co(II) complex when compared to the values of 3×10^{-13} sec for cobalt(II)–methanol[22] and 7×10^{-13} sec for Co$(H_2O)_6{}^{2+}$.[23]

The value given above for T_{1e}, which was assumed temperature independent,[22] and the other parameters reported above were then used in eq 6 and 8 to calculate the solid curves shown in Figures 3 and 5, respectively.

This interpretation of the line widths can be checked in the following manner. At the temperature where $\tau_{\mathrm{O_h}}|\Delta\omega_{\mathrm{O_h}}| = 1$, $\Delta\omega_o = P_{\mathrm{O_h}}\Delta\omega_{\mathrm{O_h}}/2$. This occurs at $10^3/T = 3.74$, Figure 3, and at this temperature $\Delta\omega_{\mathrm{O_h}} = 1/\tau_{\mathrm{O_h}} = 4.52 \times 10^5$ sec^{-1}. At this same temperature eq 8, neglecting the $P_{\mathrm{O_h}}/T_{2\mathrm{O_h}}$ term, gives $1/T_{2\mathrm{P}} = P_{\mathrm{O_h}}|\Delta\omega_{\mathrm{O_h}}|/2$ which yields $\Delta\omega_{\mathrm{O_h}} = 1/\tau_{\mathrm{O_h}} = 4.34 \times 10^5$ sec^{-1}. The good agreement of these independently determined values and the fit of the data in Figures 3 and 5 leave little doubt that the interpretation given is correct. The inequalities assumed for the derivations of the equations used are satisfied by the values obtained for $1/T_{2\mathrm{O_h}}$, $\tau_{\mathrm{O_h}}$, $\Delta\omega_{\mathrm{O_h}}$, and T_{1e}. The value obtained for $1/\tau_{\mathrm{O_h}}$ from Figure 4 at 25° is $(6.5 \pm 1.1) \times 10^6$ sec^{-1}. If the forward reaction of equilibrium 3 is assumed to be a simple dissociation process, then $1/\tau_{\mathrm{O_h}} = k_3$.

Discussion

The value calculated for ΔH of 13.0 kcal/mol for K_1 agrees very well with the values 13.3 kcal/mol reported by Farina and Swinehart[9] and 13.4 kcal/mol reported by Katzin.[2] At 38° the value calculated in this work for $[\mathrm{Co_{T_d}}^{2+}]/[\mathrm{Co_{O_h}}^{2+}]$ is 0.014 ± 0.009.[21] This does not agree very well with the value of 0.04 estimated by Katzin[2] from electronic absorption spectra. Since Katzin based his approximation on strongly overlapping absorption peaks, our result probably agrees with Katzin's result within our mutual experimental uncertainty.

The method reported here of determining equilibrium constants could be applied to any system that meets the following requirements: there must be a significant change in the concentration of the species being studied, at least one (sometimes more than one) of the species must have a measurable chemical shift, and it must be possible to relate the observed chemical shift to at least one (sometimes more than one) of the species involved in the equilibrium. All of these requirements must be met within the liquid temperature range of the solvent. It is not necessary to know the exchange rate constant if $1/\tau \gg |\Delta\omega|$, but the results can be checked for consistency if this value is known. This method is particularly valuable when the equilibrium constant cannot be accurately determined by other methods. However, caution should be exercised when extrapolating K_1 to temperatures not in the temperature range studied.

The mechanism for the octahedral–tetrahedral interconversion, as proposed by Farina and Swinehart,[9] is given by eq 2 and 3. Our results are consistent with this mechanism. Under steady-state conditions

$$k_2 = k_{-2}k_{-3}K_1/k_3 \qquad (18)$$

If it is assumed that k_{-3} approaches a bimolecular diffusion-controlled rate constant of approximately 10^9,[24] and if the value of k_{-2} of 3.1×10^3 reported by Farina and Swinehart[9] is used, a rate constant of 10^6 would be estimated for k_2 at 25° from eq 18. Without experimental determination of k_{-3} or k_2, it is impossible to estimate the undetermined kinetic values more accurately. However, the measured and estimated $\Delta H^{\ddagger}$'s and $\Delta S^{\ddagger}$'s for reactions 2 and 3 are consistent with the proposed mechanism.

Acknowledgments.—John Loudenback's assistance with some of the electrical components of the instrumentation was greatly appreciated.

---

[22] Z. Luz and S. Meiboom, *J. Chem. Phys.*, **40**, 1058 (1964).

[23] D. Fiat, Z. Luz, and B. L. Silver, *ibid.*, **49**, 1376 (1968).

[24] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1961, pp 268–272.