Compounds **3** and **6**–**9** were so used.

Typically, 0.6 mmol of metal peroxo complex was suspended in boiling methanol, benzene, toluene, or mesitylene and the stoichiometric quantity of cyclohexene added. The proton NMR spectrum of the reaction solution revealed an absorption at 3.2 ppm downfield from Me_4Si which is characteristic of the methine hydrogens of cyclohexene epoxide.

Compound **7** was dissolved in benzene along with excess styrene. After the mixture was heated for 2 h at 70 °C, the proton NMR spectrum contained narrow multiplets centered at 2.8, 3.15, and 3.85 ppm as required for styrene oxide.

Compound **7** was also employed as a catalyst in the oxidation of excess cyclohexene by *tert*-butyl hydroperoxide. Reaction was allowed to proceed for 2 h or more at 80 °C and the solution turned first blue and then brown. The proton NMR spectrum of the solution showed a peak at 3.4 ppm which was assumed to be due to the methine protons of cyclohexene epoxide.

Sheldon has observed that catalysts such as $MoO_2(acac)_2$ were converted in the course of reaction to a diol (e.g., cyclohexanediol) complex which continued to catalyze the reaction.[1f] It was assumed that acac is destroyed by the peroxide.[1c,h] However, the work of Jacobson et al.[3] suggests that if a ligand on the catalyst resists oxidation by peroxide, then such a catalyst is preserved throughout the reaction. The ligands employed in the present work are stable toward peroxide.

Photochemistry. The complexes lost oxygen over a period of weeks when they were left exposed to light. Compound **8** suspended in hexane was exposed to 3000-Å radiation in a Rayonet Srinivasan-Griffith photochemical reactor for 15 h, but no detectable decomposition occurred. However, irradiation of compounds **8** and **11** in the presence of methanol under N_2 atmosphere gave brown oxo complexes of molybdenum in a reduced valence state. The fate of the methanol was not established. This preliminary finding suggests that the use of irradiation should be examined further in an effort to increase the scope of application of peroxo complexes. Thermal conditions alone do not bring about oxidation of primary alcohols by peroxide.[3]

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Registry No. **1**, 38293-27-5; **2**, 73680-22-5; **3**, 73712-00-2; **4**, 73680-23-6; **5**, 73680-24-7; **6**, 73680-25-8; **7**, 73680-26-9; **8**, 17457-39-5; **9**, 73680-27-0; **10**, 73680-28-1; **11**, 25464-04-4; **12**, 73680-29-2; **13**, 73680-30-5; **14**, 23273-37-2; **15**, 73680-31-6; **16**, 73680-32-7; **17**, 25464-05-5; $OAs(C_4H_9)_3$, 4964-17-4; $OP(C_3H_7)_3$, 1496-94-2; $OP(C_4H_9)_3$, 814-29-9; $OAs(C_3H_7)_3$, 4964-16-3; $As(C_4H_9)_3$, 5852-58-4; $CrO_3{\cdot}ONC_5H_5$, 73680-33-8; C_5H_5NO, 694-59-7; $[MoO(O_2)_2{\cdot}OP(n\text{-}C_3H_7)_2]_2$, 73680-34-9; $[MoO_3{\cdot}As(n\text{-}C_3H_7)_2]_2$, 73680-35-0.

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Effect of Chloroform on the Relative Stabilities of the $CoCl_2(py)_2$ and $CoCl_2(py)_4$ Complexes in Solution

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The effect of varying composition of pyridine–chloroform mixtures on the $CoCl_2(py)_4 \rightleftharpoons CoCl_2(py)_2 + 2py$ equilibrium has been studied spectrophotometrically. Derived thermodynamic characteristics of the reaction show marked variations with varying composition of the mixed solvent. Separate contributions to the overall effects, viz., the thermodynamic transfer functions of the reactants, are derived from combined spectrophotometric, calorimetric, and solubility measurements. The results indicate strong specific interaction of chloroform with $CoCl_2(py)_4$ and weaker if any interaction with $CoCl_2(py)_2$. Hydrogen-bond formation of the protic solvent with the coordinated pyridine molecules cooperating with the d → π* electron delocalization is proposed as a possible explanation of the effects observed.

Introduction

The effect of noncoordinating solvents on coordination equilibria has not, so far, received any broader interest, probably being considered to be of second-order importance. However, there are indications that in certain systems strong specific interactions may occur between well-defined solution complexes and protic solvents not entering the first coordination spheres. An example is provided by the H···π type interaction of haloforms with the $Co(NCS)_2(\gamma\text{-pic})_4$ complex, as reported by Narbutt and Siekierski.[1,2] Recently, we found that chloroform and, to a smaller extent, 1,2-dichloroethane exert a stabilizing effect on the $MCl_2(py)_4$ type complexes as well.[3] The effect being stronger for $NiCl_2(py)_4$ than for $MnCl_2(py)_4$ indicated that ability of the coordinated pyridine molecules to act as proton acceptors may be controlled by the d_π electron back-donation from the central metal atom. It also seemed necessary that the two effects, viz., the d_π electron back-donation from the central metal atom to the amine molecules and the π···H interaction of the latter with the protic solvent, should be cooperative, enhancing each other. If real, the combined effect should critically depend on the symmetry of the complex, thus resulting in preferential stabilization of certain arrangements of the respective ligands around the central metal atom against others. In accordance with this expectation, chloroform additions to pyridine were found to displace equilibrium 1 toward the octahedral complex

$$CoCl_2(py)_4 \rightleftharpoons CoCl_2(py)_2 + 2py \qquad (1)$$

$CoCl_2(py)_4$, despite sharply decreasing pyridine activity.[4] Similarly, transformation of the $CuCl_2(py)_3$ pentacoordinate complex into $CuCl_2(py)_4$ was found to take place upon chloroform additions to pyridine.[5] It seems that these are but

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0020-1669/80/1319-2259$01.00/0

special manifestations of the more general effect of cooperation of the d_π electron back-donation from the central metal atom to the coordinated ligands with the $\pi\cdots H$ type interaction of the latter with protic solvents.

The aim of the present work is to examine the effect of the protic solvent chloroform on the configurational equilibrium (eq 1). The equilibrium was earlier studied by other authors[6-9] but not from the viewpoint of solute–solvent interactions. Variations in the solvent activity coefficients of the complexes involved were taken into account in our studies,[10-13] but no specific effects were observed in the aprotic diluents then used. An attempt will presently be made at separating the overall protic solvent effect on equilibrium 1 into its separate contributions, viz., the thermodynamic transfer functions of the reactants.

Experimental Section

Crystalline $CoCl_2{\cdot}2py$ (violet form) was deposited from the ethanolic solution of anhydrous cobalt(II) chloride, to which a small amount of pyridine was added.[14,15] The product was purified by repeated crystallizations from ethanol and finally from chloroform, both containing a small amount of pyridine added. It was then dried in air and stored in a desiccator. The pink tetrapyridinate, $CoCl_2{\cdot}4py$, was obtained anologously by using 1:1 ethanol + pyridine or, in the last operation, chloroform + pyridine mixtures. The stoichiometry of the $CoCl_2{\cdot}2py$ compound used in the calorimetric work was checked by the standard EDTA titrimetric determination of cobalt(II). Special care was taken to obtain a good quality chloroform. The reagent-grade product was shaken with concentrated sulfuric acid to remove ethanol, washed with water until neutrality was attained, dried over K_2CO_3, and subsequently distilled from over Linde 4A molecular sieve through a 30-plate column. Pyridine was dried by means of KOH pellets and finally distilled through the column also using Linde 4A molecular sieve.

Solubilities were determined by using the saturating column method described previously.[12] Weighed portions of the saturated solutions were analyzed for cobalt by standard EDTA titrations. Molar concentrations of the solutions were calculated taking into account the densities determined independently. The same methods were used in the determination of concentrations of solutions used in the spectrophotometric work. Absorption spectra were measured by using a Zeiss VSU-2 spectrophotometer equipped with a thermostated cell compartment. The temperature of the solutions was measured by using a termistor located in the cell.

Heats of solution of the $CoCl_2{\cdot}2py$ (violet form) and $CoCl_2{\cdot}4py$ solid compounds were determined by using a reaction calorimeter of our own construction, described previously.[16,17]

Results and Discussion

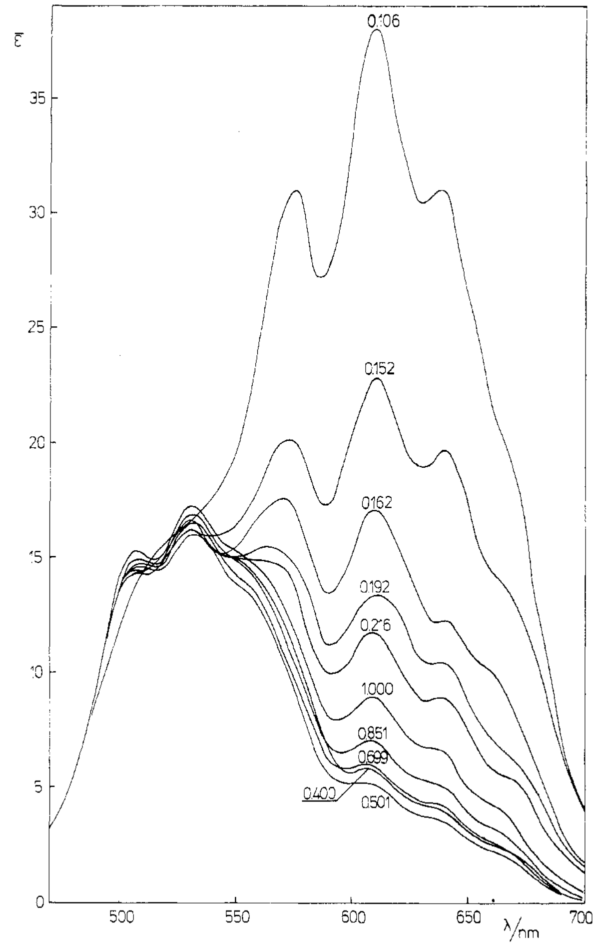

Figure 1. Visible absorption spectra of $CoCl_2$ in pyridine–chloroform mixtures at 25 °C; mole fractions of pyridine are indicated.

Effects in the Visible Spectrum. It has been well established that $CoCl_2$ dissolved in pyridine exists mainly in the form of the $CoCl_2(py)_4$ pseudooctahedral complex,[11] exhibiting a weak absorption band with maximum at 525 nm corresponding to the ${}^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$ transition.[18] The $CoCl_2(py)_2$ pseudotetrahedral complex, though present in but a small proportion at room temperature, contributes significantly to the measured spectrum above some 550 nm. Its structured absorption band corresponding to the ${}^4T_1(P) \leftarrow {}^4A_2(F)$ transition in regular tetrahedral symmetry[18] exhibits three-component absorption maxima at approximately 580, 610, and 640 nm and a shoulder at approximately 670 nm. Increasing temperature results in a rapid increase in intensity of the lower energy band, indicating increasing concentration of the tetrahedral complex formed in a strongly endothermic reaction. Additions of a diluent normally result in similar changes owing to decreasing pyridine activity.[10,11] Exceptional in this respect appears to be chloroform, whose additions to pyridine initially induce the opposite effect, despite sharply decreasing pyridine activity.[3] Illustration is provided by the spectra shown in Figure 1. This effect has not been noticed in the earlier works, in which the relatively dilute solutions of pyridine in chloroform were used.[8] It is only at high chloroform contents, corresponding to $x_{py} < 0.4$, that further decrease in pyridine activity results in a rapid increase in intensity of the band due to the tetrahedral complex. The limiting intensity of the band, corresponding to $\epsilon_{max} = 610$, is attained at pyridine concentrations decreasing down to that of $CoCl_2$, viz., approximately 0.001 M, corresponding to the mole fraction of pyridine of approximately 10^{-4}. Up to this moment, both positions of the component bands and their relative intensities remain constant. At still lower pyridine concentrations some irreproducible changes in the spectrum occur. The origin of this latter effect

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is not clear yet, although it has been discovered already in the early work by Nelson et al.[8]

Another interesting effect visualized in Figure 1 consists in slightly decreasing intensity of the higher energy band, concomitant with decreasing intensity of the "blue" band of the $CoCl_2(py)_2$ complex, observed within the range of lower chloroform contents. It might be considered as contradicting the assumption of the two-species equilibrium (1). However, it almost certainly exists in the influence chloroform exerts on the absorption intensity due to the $CoCl_2(py)_4$ single complex, as a similar effect is observed in the spectrum of the $NiCl_2(py)_4$ analogous complex.[3] The effect is not particularly puzzling in view of the strong interactions between chloroform and the octahedral complexes indicated by the present results.

Evaluation of Spectrophotometric Results. The solvent-independent equilibrium constant of reaction 1 may be defined as

$$K^\circ = c_2 y_2^\circ a_{py}^2 / c_4 y_4^\circ \tag{2}$$

where c_2 and c_4 denote equilibrium concentrations of the $CoCl_2(py)_2$ and $CoCl_2(py)_4$ complexes, respectively, y_2° and y_4° are the solvent activity coefficients of the complexes, and a_{py} is the activity of pyridine. The concentration-dependent activity coefficients of the complexes have been disregarded in this definition of the equilibrium constant as being close to unity, since the complexes are neutral and their concentrations in the solutions studied were low. On the other hand, under conditions of the present work most essential were variations in the solvent activity coefficients. The latter may generally be defined as

$$y_i^\circ = \exp(\mu_i^\circ - \mu_i^{\circ *})/RT \tag{3}$$

where

$$\mu_i^\circ = \lim_{c_i \to 0}(\mu_i - RT \ln c_i) \tag{4}$$

μ_i and c_i being the chemical potential and concentration of the ith solution species, respectively, and $\mu_i^{\circ *}$ denoting the value of μ_i°, the standard chemical potential of the species, in pure pyridine. It follows that $y_i^\circ \to 1$, as $x_{py} \to 1$, x_{py} denoting mole fraction of pyridine in the mixed solvent. Choosing solutions in pyridine as the reference states has the advantage of a good reproducibility of the measured quantities, while a worse reproducibility is achieved for solutions in chloroform.

It follows from eq 2 that

$$-RT \ln K = \Delta G^{\circ *} + \Delta G^\circ_{tr}(2) - \Delta G^\circ_{tr}(4) + 2RT \ln f_{py} \tag{5}$$

where

$$K = c_2 x_{py}^2 / c_4 \tag{6}$$

may be considered as the thermodynamic equilibrium constant of reaction 1 defined for the given mixed solvent as the reference medium in the definition of the solvent activity coefficients, $\Delta G^{\circ *} = -RT \ln K^\circ$

$$\Delta G^\circ_{tr}(2) = RT \ln y_2^\circ \tag{7}$$

and

$$\Delta G^\circ_{tr}(4) = RT \ln y_4^\circ \tag{8}$$

are the standard Gibbs free energies of transfer from pyridine to the given mixed solvent of the $CoCl_2(py)_2$ and $CoCl_2(py)_4$ complexes, respectively, and f_{py} is the mole fraction scale activity coefficient of pyridine. The other relation of importance for our purposes is

$$RT^2 \frac{d \ln K}{dT} = \Delta H^{\circ *} + \Delta H^\circ_{tr}(2) - \Delta H^\circ_{tr}(4) + 2\Delta H^\circ_{tr}(py) \tag{9}$$

where $\Delta H^{\circ *}$ is the standard enthalpy change of reaction 1 occurring in pyridine, and

$$\Delta H^\circ_{tr}(2) = -RT^2 \frac{d \ln y_2^\circ}{dT} \tag{10}$$

$$\Delta H^\circ_{tr}(4) = -RT^2 \frac{d \ln y_4^\circ}{dT} \tag{11}$$

$$\Delta H^\circ_{tr}(py) = -RT^2 \frac{d \ln f_{py}}{dT} \tag{12}$$

are the standard enthalpies of transfer of the species indicated.

It is clear from eq 9 that

$$\Delta H^\circ = RT^2 \frac{d \ln K}{dT} \tag{13}$$

represents the true heat of reaction (1) for a fixed solvent composition. It will be seen further that calorimetry does not permit determination of the enthalpy change of reaction 1 at a fixed solvent composition, so that derivation of d ln K/dT from the spectrophotometric results provides the only possible way of arriving at this quantity.

In calculations of K, use is made of the relation

$$\frac{c_2}{c_4} = \frac{\bar{\epsilon} - \epsilon_4}{\epsilon_2 - \bar{\epsilon}} \tag{14}$$

where $\bar{\epsilon}$ denotes the mean molar absorption coefficient of cobalt(II) measured within the spectral range in which light absorption due to the $CoCl_2(py)_2$ tetrahedral complex predominates, ϵ_2 is the molar absorption coefficient of the latter complex, and ϵ_4 is the molar absorption coefficient of the $CoCl_2(py)_4$ complex at the given wavelength. The necessary values of ϵ_2 (610 M^{-1} cm^{-1} at 610 nm, and 490 M^{-1} cm^{-1} at 640 nm) were found from the limiting spectrum of $CoCl_2$ at the very lowest pyridine concentrations in chloroform, as mentioned in the preceding section. On the other hand, values of ϵ_4 at 610 and 640 nm, 1.4 and 0.8, respectively, found in our previous work by an extrapolation procedure from the temperature dependence of the absorbance,[11] were used in the present calculations. Since ϵ_4 was usually very small compared with $\bar{\epsilon}$, its precise knowledge was not very important. As a result, the small expected variations in ϵ_4 with varying solvent composition were altogether unimportant for the present calculations. We may note that values of c_2/c_4 resulting at the above two wavelengths were consistent at all solvent compositions and at all the temperatures studied to within some 5%. Thus derived values of K were used in the calculations of $\Delta G^\circ = -RT \ln K$, the standard Gibbs free energy changes of reaction 1 at fixed mixed solvent composition. On the other hand, plots of ln K vs. $1/T$, shown in Figure 2, served for the derivation of the ΔH° values using the least-squares linear approximations. The derived reaction heats and standard free energies are listed in Table I.

Phase Equilibria

Figure 3 shows the solubility isotherm of cobalt(II) chloride in pyridine + chloroform mixtures, indicated being stoichiometries of the solid phases in equilibrium. As for other pyridine + diluent mixtures,[10,11] the $CoCl_2\cdot 2py$ and $CoCl_2\cdot 4py$ solid complexes are stable within low and high pyridine contents, respectively. However, a third solid phase is also formed in this system, stable within the intermediate composition range. It decomposes rapidly being removed from the liquid phase, but its stoichiometry of $CoCl_2\cdot 4py\cdot CHCl_3$ clearly follows from the 20.98% loss in weight ($CoCl_2\cdot 4py\cdot CHCl_3$ requires 21.10%) when crystals equilibrated with an approximately 1:1 pyridine–chloroform mixture are transferred in a weighing boat to a desiccator containing pure pyridine. Unfortunately, reproducibility of solubility measurements corresponding to the

Table I. Thermodynamic Characteristics (in kJ/mol units) of Reaction 1 in Pyridine–Chloroform Mixtures of Varying Composition; at 25 °C

mole fraction of py	10^4K^a	$\Delta G°$	$\Delta H°$	$\Delta G°_{tr}(4)$	$\Delta G°_{tr}(2)^c$	$\Delta H°_{tr}(4)$		$\Delta H°_{tr}(2)^g$
						d	*e*	
1	123 ± 10	10.9 ± 0.2	56.9 ± 1.0	0	0			0
0.940	105 ± 9	11.3 ± 0.2	57.9 ± 0.3	−0.15	0.26	−0.8	−0.9 ± 0.4	0.2 ± 1.7
0.907	125 ± 10	10.9 ± 0.2	61.1 ± 0.7	−0.27	0.29	−1.6	−1.4 ± 0.4	2.6 ± 2.1
0.851	65 ± 7	12.5 ± 0.3	61.2 ± 0.7	−0.51	1.12	−2.1	−2.3 ± 0.5	2.3 ± 2.1
0.699	34 ± 4	14.1 ± 0.3	66.5 ± 0.8	−1.42	1.99	−5.0	−4.6 ± 0.9	5.3 ± 2.2
0.600	23 ± 3	15.1 ± 0.3	68.7 ± 0.7	−2.20	2.69	−7.6	−6.2 ± 2.2	5.8 ± 2.1
0.501	15 ± 2	16.2 ± 0.3	71.1 ± 0.4	−3.17	3.31	−10.7		6.6 ± 1.8
0.499	17 ± 2	15.8 ± 0.3	68.2 ± 1.3	−3.17	2.98	−10.9		3.6 ± 2.7
0.403	13 ± 2	16.5 ± 0.3	69.4 ± 0.6			−16.2		−0.1 ± 2.0
0.400	12 ± 2	16.7 ± 0.3	67.8 ± 0.9			−16.3		−1.5 ± 2.3
0.295	8.5 ± 0.8	17.5 ± 0.2	68.2 ± 0.8			−23.3		−4.0 ± 2.2
0.242	7.6 ± 0.7	17.8 ± 0.2	67.4 ± 0.7			−26.3		−6.2 ± 2.1
0.160	7.9 ± 0.6	17.7 ± 0.2	64.0 ± 1.6			−28.2		−9.2 ± 3.0
0.152	8.7 ± 0.6	17.5 ± 0.2	68.0 ± 0.8			−27.3		−4.1 ± 2.2
0.083	9.2 ± 0.6	17.4 ± 0.2	61.1 ± 1.6			−30.6		−12.6 ± 3.0
0.082	6.4 ± 0.4	18.3 ± 0.2	65.7 ± 0.4			−29.0		−6.4 ± 1.8
0 + 0.03			59.6 ± 1.9^b				^{f}	
0.846							−1.1	
0.756							−3.4	
0.500							−11.7	

[a] As defined by eq 6. [b] From calorimetric heats of solution of $CoCl_2\cdot 2py$ (see Table II) calculated from eq 19. [c] Calculated from eq 5. [d] Calculated from eq 20 from combined calorimetric and spectrophotometric data (probable error estimated as not higher than ±0.4 kJ/mol). [e] From solubility and spectrophotometric data calculated from eq 16. [f] From calorimetric heats of solution of $CoCl_2\cdot 4py$ calculated as $\Delta H°_{tr}(4) = \Delta H°_s(4) - \Delta H°*_s(4)$. [g] Calculated from eq 17.

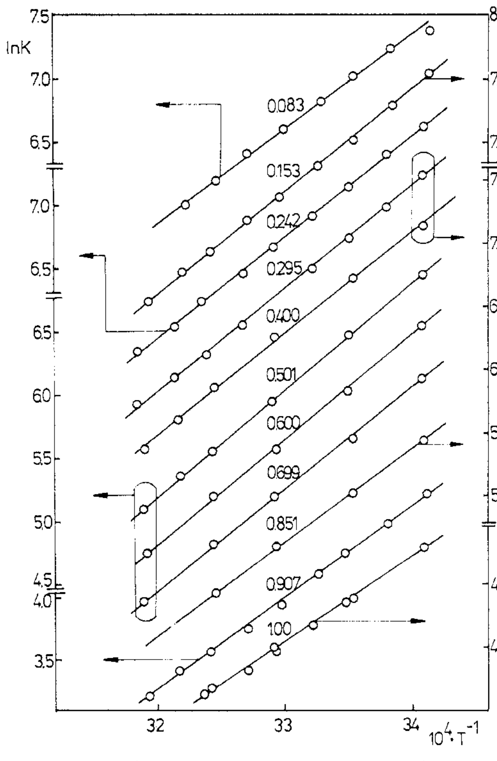

Figure 2. ln K vs. $1/T$ plots for reaction 1 in pyridine–chloroform mixtures of varying composition; mole fractions of pyridine are indicated.

chloroform-containing solid phase was not satisfactory, so that they could not be used for the derivation of thermodynamic quantities. On the other hand, the solubility data for $CoCl_2\cdot 4py$ were evaluated by using relations 15 and 16:

$$y_4° = S_4^*/S_4 \qquad (15)$$

$$\Delta H°_{tr}(4) = RT^2 \frac{d \ln S_4/S_4^*}{dT} \qquad (16)$$

where S_4 and S_4^* denote equilibrium concentrations of the $CoCl_2(py)_4$ complex in saturated solutions in the given mixed solvent and in pure pyridine, respectively. By use of the spectrophotometrically determined equilibrium quotient, c_2/c_4, of reaction 1, values of S_4 were found as $S_4 = \bar{S}/(1 + c_2/c_4)$, where $\bar{S}$ denotes total solubility. Resulting values of $\Delta G°_{tr}(4) = RT \ln y_4°$ and of $\Delta H°_{tr}(4)$ are listed in Table I and plotted in Figures 4 and 5. The full lines in Figure 4 represent the earlier determined free energies of transfer of the $MnCl_2(py)_4$ and $NiCl_2(py)_4$ complexes. As is seen, the curve for $CoCl_2(py)_4$ determined down to $x_{py} = 0.5$ is intermediate between those for the two analogous complexes. On the assumption that the same is true within the range of lower pyridine contents as well, the other part of the $\Delta G°_{tr}(4)$ vs. x_{py} curve for the $CoCl_2(py)_4$ complex has been calculated from the data for $MnCl_2(py)_4$ and $NiCl_2(py)_4$. The free energies of transfer of the $CoCl_2(py)_2$ tetrahedral complex were than calculated from

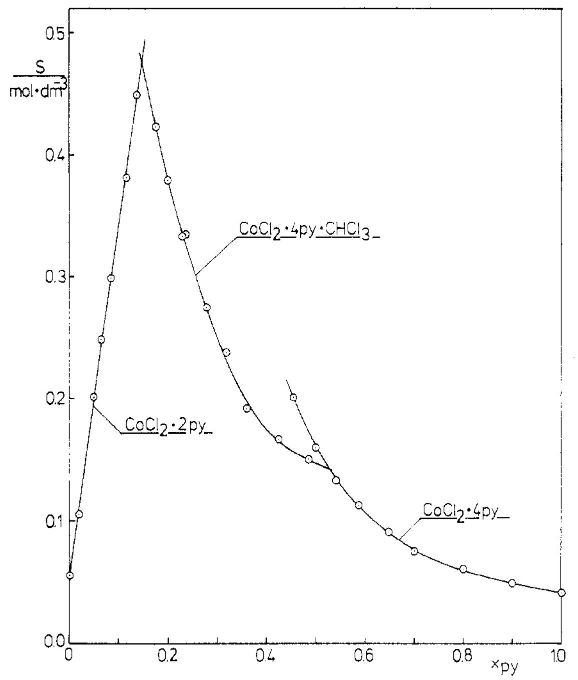

Figure 3. Solubility isotherm of $CoCl_2$ in pyridine–chloroform mixtures at 25 °C; stoichiometries of the solid phases in equilibrium are indicated.

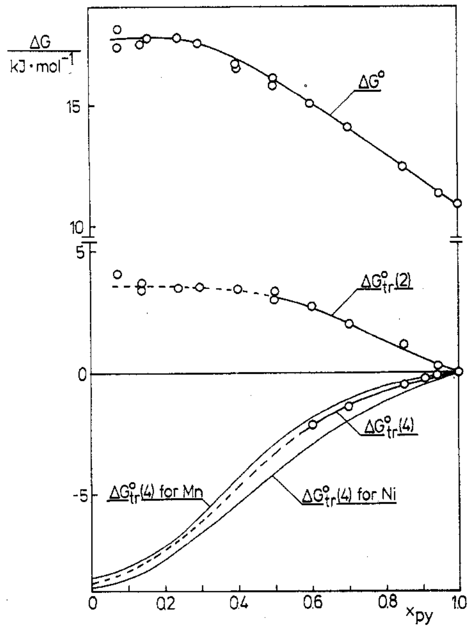

Figure 4. Variations of the standard free energy of reaction 1 as defined by eq 5 and 6 and of the free energies of transfer of the $CoCl_2(py)_2$ and $CoCl_2(py)_4$ complexes with varying composition of pyridine–chloroform mixtures at 25 °C; the free energies of transfer for the $MnCl_2(py)_4$ and $NiCl_2(py)_4$ complexes are indicated.

eq 5 using the pyridine activity data of ref 3. Respective plots are shown in Figure 4, the broken sections of the curves representing respective dependences estimated by using the data for $MnCl_2(py)_4$ and $NiCl_2(py)_4$.

Calorimetric Results

It may be readily shown that

$$\Delta H^\circ{}_s(2) - \Delta H^{\circ*}{}_s(2) = \Delta H^\circ{}_{tr}(2) - \alpha\Delta H^\circ + \alpha^*\Delta H^{\circ*} \qquad (17)$$

where $\Delta H^\circ{}_s(2)$ and $\Delta H^{\circ*}{}_s(2)$ denote the directly measured heats of solution of the $CoCl_2{\cdot}2py$ solid compound in the given mixed solvent and in pure pyridine, respectively, and α and α^* are corresponding degrees of formation of the $CoCl_2(py)_4$ solution complex. At the same time, the reaction heats are interrelated by

$$\Delta H^\circ = \Delta H^{\circ*} + \Delta H^{\circ*}{}_{tr}(2) + 2\Delta H_{tr}(py) - \Delta H^\circ{}_{tr}(4) \qquad (18)$$

It follows that it is impossible to derive the required heat of reaction 1 from the heat of solution data without the simplifying assumption that the enthalpies of transfer are independent of solvent composition over a certain composition range. There is a chance that the approximation will be good enough for a narrow range of low pyridine contents in the mixed solvent where the degree of formation of the octahedral complex steeply increases with increasing pyridine concentration. It follows from eq 17 that the approximate relation, 19, will then be valid, where prime and double prime relate

$$\Delta H^\circ{}_s(2)'' - \Delta H^\circ{}_s(2)' = (\alpha' - \alpha'')\Delta H^\circ \qquad (19)$$

to two different pyridine contents in the mixed solvent, and ΔH° denotes the assumed constant reaction heat in the respective composition range of the reaction medium. On the other hand, the calorimetrically determined $\Delta H^\circ{}_s(2)$ values coupled with the spectrophotometrically determined reaction heats enable, at least in principle, one to derive variations in both $\Delta H^\circ{}_{tr}(2)$ and $\Delta H^\circ{}_{tr}(4)$, provided that $\Delta H_{tr}(py)$ is known. Evaluation of the heats of solution of the tetrapyridinate, $CoCl_2{\cdot}4py$, proceeds along similar lines, except that the term $2\Delta H_{tr}(py)$ appears in an equation analogous to (17). Neglecting the influence of the solutes, the necessary heats of

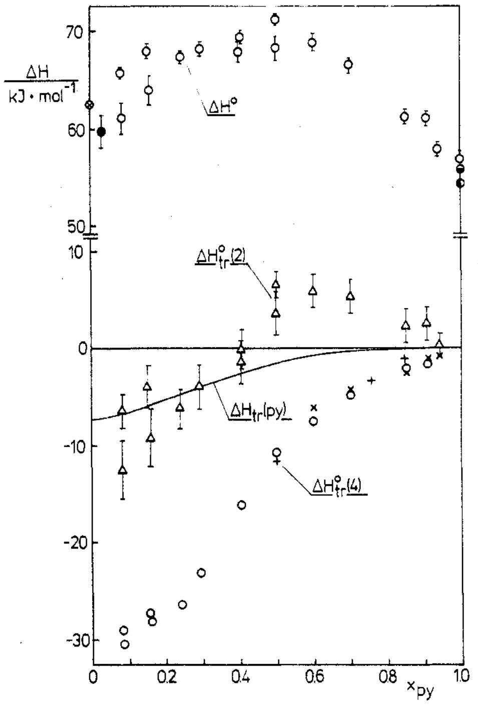

Figure 5. Variations of the reaction heat and of the heats of transfer of reactants and products of reaction 1 with varying composition of pyridine + chloroform mixtures at 25 °C. Heats of reaction 1: (○) values derived from temperature dependence of the equilibrium constant; (●) average calorimetric value for mole fractions of pyridine varying up to 0.03; (⊗) calorimetric value of Nelson et al.[8] (pyridine concentrations low); (◒ and ◐) values derived from temperature dependence of equilibrium constant in ref 7 and 9, respectively. Heats of transfer: (△) heats of transfer of $CoCl_2(py)_2$ calculated from eq 17; (○) heats of transfer of $CoCl_2(py)_4$ calculated from the calorimetric heats of solution of $CoCl_2{\cdot}2py$ using eq 20; (×) heats of transfer calculated from the temperature dependence of solubility of $CoCl_2{\cdot}4py$ using eq 16; (+) heats of transfer from calorimetric heats of solution of $CoCl_2{\cdot}4py$; (full line) heats of transfer of pyridine calculated from the data of Becker et al.[19]

transfer of pyridine can be calculated as $\Delta H_{tr}(py) = H^M + (1 - x_{py})dH^M/dx_{py}$ from the heat of mixing data for the binary system pyridine–diluent, and the data reported by Becker et al.[19] were used for this purpose.

The heats of solution of $CoCl_2{\cdot}2py$ violet form are listed in Table II, along with the degrees of formation of the octahedral complex, determined spectrophotometrically by using relation 14 on the assumption that $c_2 + c_4 = c$. Included are some heats of solution of the tetrapyridinate, $CoCl_2{\cdot}4py$, determined both from calorimetry and from the temperature dependence of solubility. The reaction heat at small pyridine concentrations ($x_{py} < 0.05$) calculated from eq 19 has the value of 59.6 ± 1.9 kJ/mol and agrees reasonably with the reaction heats derived from the temperature dependence of the equilibrium constant at higher pyridine contents in the mixed solvent. Nelson's reported value is somewhat higher (15.2 kcal/mol = 63.60 kJ/mol) but still remains within the uncertainty limits of the spectrophotometric results. The latter were used in the calculation of the heats of transfer of the complexes involved in reaction 1 listed in Table I. It follows from eq 17 that the derived value of $\Delta H^\circ{}_{tr}(2)$, the enthalpy of transfer of the $CoCl_2(py)_2$ complex, will critically depend on the possible errors involved in the "spectrophotometric" reaction heats, ΔH° and $\Delta H^{\circ*}$, since α is large (>0.95) over the most part of the entire solvent composition range. As a result, accurate

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Table II. Heats of Solution, $\Delta H^\circ_s(2)$ and $\Delta H^\circ_s(4)$, of the $CoCl_2 \cdot 2py$ (Violet Form) and $CoCl_2 \cdot 4py$ Solid Compounds, Respectively, in Pyridine–Chloroform Mixtures at 25 °C (in kJ mol^{-1})

x_{py}	α^a	$\Delta H^\circ_s(2)$	$\Delta H^\circ_s(4)$	x_{py}	α^a	$\Delta H^\circ_s(2)$
1.0		−32.06 ± 0.18	12.67 ± 0.06	0.499		−40.6
			11.5 ± 0.3^b			
				0.393	0.995	−43.0
0.903			9.9 ± 0.4^b			
				0.351	0.99	−43.8
0.846			11.6			
				0.222	0.985	−48.8
0.831	0.99	−35.2		0.121	0.95	−45.5
0.799			8.1 ± 0.5^b			
				0.050	0.79	−36.5
0.756			9.3			
				0.033	0.63	−17.7^c
0.731		−36.3				
				0.021	0.42	−6.1^c
0.706			6.8 ± 0.9^b			
				0.011	0.21	+8.2^c
0.613	0.993	−37.5				
				0.004	0.075	+14.9^c
0.606			4.8 ± 2.2			
0.500			1.0			

[a] α denotes degree of formation of $CoCl_2(py)_4$ in solution determined spectrophotometrically. [b] From the temperature dependence of solubility of $CoCl_2 \cdot 4py$, all the other results are obtained calorimetrically. [c] Used in calculation of ΔH° at small pyridine concentrations.

values of $\Delta H^\circ_{tr}(2)$ could not be obtained from the present results. On the other hand, combination of eq 17 and 18 gives

$$\Delta H^\circ_{tr}(4) = \Delta H^\circ_s(2) - \Delta H^{\circ *}_s(2) - (1-\alpha)\Delta H^\circ + (1-\alpha)\Delta H^{\circ *} + 2\Delta H_{tr}(py) \quad (20)$$

from where it follows that possible errors in ΔH° and $\Delta H^{\circ *}$ would have a relatively small influence on $\Delta H^\circ_{tr}(4)$. The estimated uncertainty limits in the derived heats of transfer are indicated in Figure 5. Agreement of the data for the $CoCl_2(py)_4$ solution complex derived from the heat of solution of two different solid compounds, viz., $CoCl_2 \cdot 2py$ and $CoCl_2 \cdot 4py$, provides a nice confirmation of reliability of the heats of transfer for this complex.

Discussion

An extensive study on configurational equilibria generally formulated as

$$CoL_2X_2 + 2L \rightleftharpoons CoL_4X_2 \quad (21)$$

where L is a heterocyclic amine, e.g., pyridine or substituted pyridine, and X denotes a halide or a pseudohalide anion, was published by Nelson et al. in 1963.[8] Chloroform and nitromethane were used as solvents, and the basic thermodynamic characteristics of the reactions were derived from combined calorimetric and spectrophotometric results. The reaction entropies, found to be of predominant importance in determining position of the equilibria, were interpreted in terms of hindered rotation of the coordinated pyridine or other heterocyclic amine molecules in octahedral complexes. The d → π^* electron back-donation from the central metal atom to the amine molecules, controlled by the nature of the anionic ligand X and assumed to occur in octahedral complexes but not in the tetrahedral ones, provided a consistent explanation of the entropy data. The assumption was however made that changing solvation on passing from reactants to products does not contribute significantly to the derived thermodynamic parameters of the reactions.

A different point of view was represented by Graddon and Watton, who attached more significance to the reaction enthalpies and considered interaction between the nonbonding electron pairs to be the major factor determining coordination number of the central metal atom.[20]

Apart from the fact that Nelson's concept of d → π^* electron back-donation in octahedral complexes of the above mentioned type has now been well established,[21] the present results show that solvation effects cannot be disregarded in the interpretation of thermodynamic parameters of configurational equilibria of type (21). As already mentioned, chloroform additions to pyridine affect position of equilibrium 1 in a way indicating marked relative stabilization of the octahedral complex. The overall thermodynamic characteristics of this solvent effect, as represented by the ΔG° vs. mole fraction of pyridine plot shown in Figure 4, considerably differs from what is observed for aprotic diluents not interacting specifically with the complexes involved in reaction 1.[4,11] The free energy of transfer results (Figure 4) reveal opposite effects of chloroform on the complexes, $CoCl_2(py)_4$ being stabilized and $CoCl_2(py)_2$ destabilized by chloroform additions to pyridine. The former effect is analogous to the effects recently observed for the $NiCl_2(py)_4$ and $MnCl_2(py)_4$ pseudooctahedral complexes. However, it is only the enthalpies of transfer that reveal the real strength of the interaction of chloroform with the $CoCl_2(py)_4$ complex, approaching some 8 kJ/mol per single pyridine molecule in the coordination sphere. The entropic contribution to the overall change in solvation of the $CoCl_2(py)_4$ complex to a large extent counterbalances the enthalpic one, its standard entropy of transfer from pyridine to chloroform amounting to −72.2 J/(K mol). Less clear is the solvation behavior of the $CoCl_2py_2$ tetrahedral complex. Curiously, its enthalpies of transfer are positive for the pyridine richer mixtures and negative for those containing chloroform in excess to the 1:1 mole ratio. This might indicate that under conditions of pyridine deficiency $CoCl_2(py)_2$ would interact specifically with the protic solvent chloroform, while it prefers interacting with pyridine in the pyridine-richer mixtures. However, in neither case is the interaction as strong as that of the $CoCl_2(py)_4$ complex with chloroform. We refrain from any further speculations as to the possible nature of the interactions of $CoCl_2(py)_2$ with the solvent components, as there are large uncertainties in the derived heats of transfer for this complex. On the other hand, a more detailed discussion of molecular interactions seems to be possible for the $CoCl_2(py)_4$ octahedral complex for which the transfer functions have been determined with a good accuracy.

In interpretation of the thermodynamic transfer functions, two main contributions should be taken into consideration, in accordance with the basic concepts underlying the scaled particle theory.[22] One is due to cavity formation and the other to the interaction of the solute molecule accommodated in the cavity with the solvent around it, both considered as differences of respective quantities between the initial and final solvent media. In the present discussion we neglect the first contributions to the measured transfer functions, as the magnitudes of the latter indicate predominant importance of specific interactions of the $CoCl_2(py)_4$ complex with the protic solvent chloroform. We note, in this connection, that the free energies of transfer of the analogous $NiCl_2(py)_4$ complex from pyridine to a number of aprotic diluents were found to roughly obey expectations arising from the regular solution theory, thus indicating absence of any stronger specific interactions of the complex with pyridine.[3] Close similarity in behavior between the two complexes implies that the same should be true for $CoCl_2(py)_4$. Further, it seems almost certain that it is the coordinated pyridine molecules and not the chloride anions of the $CoCl_2(py)_4$ complex that are involved in the interaction

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with chloroform, as no indications of a stabilizing effect of chloroform on octahedral chloro complexes of either cobalt(II) or nickel(II) are observed in the other donor solvents like acetonitrile or dimethyl sulfoxide. In addition, it would be difficult to understand the above discussed different behaviors of the $CoCl_2(py)_4$ and $CoCl_2(py)_2$ complexes, if the coordinated chloride anions, and not the pyridines, were involved in the interaction with chloroform.

It seems that a consistent explanation of the present results is possible on the assumption that chloroform interacts via the $H\cdots\pi$ type bonds with the coordinated pyridine molecules, while the π-electron density on the latter is controlled by the $d \rightarrow \pi^*$ electron delocalization. Although symmetry considerations do not preclude proper d_π–p_π orbital overlap in tetrahedral coordination, conditions for d_π electron back-donation in the latter are likely to be worse than in the octahedral one.[23–25] This would explain the observed relative stabilization of the $CoCl_2(py)_4$ octahedral complex by the protic solvent chloroform, on the assumption that the $d \rightarrow \pi^*$ electron delocalization cooperates with the $\pi\cdots H$ interaction of the complex with the solvent. As already mentioned, chloroform additions to pyridine containing dissolved $CuCl_2$ were recently found to induce transformation of the $CuCl_2py_3$ square-pyramidal complex into the $CuCl_2(py)_4$ octahedral one. Since conditions for the $d \rightarrow \pi^*$ electron delocalization in an out-of-plane square-pyramidal complex certainly are worse than in an octahedral one, the latter effect likewise might be ascribed to the cooperative effect of $d \rightarrow \pi^*$ electron delocalization and the $\pi\cdots H$ type interaction of the complex with the protic solvent. On the basis of those observations, we seem to be justified in claiming that protic solvents like chloroform may induce stereochemical effects in transition-metal complexes involving heterocyclic aromatic amines as ligands.

Importance of the $d \rightarrow \pi^*$ electron delocalization in determining interaction of complexes of the above type with chloroform may also be inferred from a comparison of the heats of transfer of the $CoCl_2(py)_4$ complex with that of the "free" pyridine. The latter, calculated from the heat of mixing data of Becker et al.[19] in Figure 5 are indicated by the full line. We note, that directly comparable with the heat of transfer of the complex only is the heat of transfer of pyridine from its pure liquid to the pure chloroform, as it is only then that the standard states become comparable.[26] As is seen, the heat of transfer of four pyridine molecules only approaches that of the $CoCl_2(py)_4$ complex as pure chloroform is approached, despite the fact that the "free" pyridines act not only as π-type but primarily as the n-type bases.[27] It becomes clear that the pyridine molecules in the complex aquire additional π-electron density as a result of their interaction with the central metal atom. Further support for the above claimed dependence of the $H\cdots\pi$ type interaction between the complex and a protic solvent on the $d \rightarrow \pi^*$ electron delocalization is provided by the fact, visualized in Figure 4, that the stabilizing effect of chloroform on the MCl_2py_4 type complexes increases in the order Mn(II) < Co(II) < Ni(II), thus in the order of increasing number of d_π electrons of the central metal atom.

Registry No. $CoCl_2(py)_4$, 13985-87-0; $CoCl_2(py)_2$, 14024-92-1.

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Trans Effect in Octahedral Complexes. 4. Kinetic Trans Effect Induced by the S-Bonded Thiosulfato Ligand in Bis(ethylenediamine)cobalt(III) Complexes[1–3]

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The new complex *trans*-$[(en)_2Co(OH_2)(S_2O_3)]^+$ has been prepared by stoichiometric oxidation of *trans*-$[(en)_2Co(S_2O_3)_2]^-$ with I_3^-, $\Delta([(en)_2Co(S_2O_3)_2]^-)/\Delta(I_3^-) = 2.08 \pm 0.06$, and has been characterized by a variety of indirect techniques. This complex contains S-bonded thiosulfate situated trans to a reasonably labile water ligand and is therefore a suitable substrate for investigation of the sulfur-induced kinetic trans effect (KTE). The pK_a of the trans water ligand is 7.4 ± 0.1. The rate law governing anation by SCN^- or NO_2^- to yield the characterized complexes *trans*-$(en)_2Co(L)(S_2O_3)$ is rate = $k[(en)_2Co(OH_2)(S_2O_3)^+][L^-]$; at 26.4 °C, $\mu = 1.00$ M ($LiClO_4$), $k_{SCN} = 0.040$ (2) and $k_{NO_2} = 0.046$ (2) $M^{-1}\ s^{-1}$, $\Delta H^*_{SCN} = 14.5$ (5) and $\Delta H^*_{NO_2} = 13.8$ (5) kcal/mol, and $\Delta S^*_{SCN} = -17$ (2) and $\Delta S^*_{NO_2} = -19$ (2) eu. Through comparisons with literature data these results show (1) S-bonded $S_2O_3^{2-}$ is a relatively efficient trans-labilizing group, substitution trans to $S_2O_3^{2-}$ occurring ca. 2×10^4 times faster than substitution trans to NH_3, (2) the KTE induced by S-bonded SO_3^{2-} on H_2O is ca. 5×10^3 times larger than that induced by S-bonded $S_2O_3^{2-}$, and (3) the KTE series for ligands S-bonded to cobalt(III) is $SO_3^{2-} > RSO_2^- > S_2O_3^{2-}$ in exact correspondence with the structural trans effect (STE) series determined for these ligands. Thus, the lability of the ligand situated trans to sulfur (KTE) is highly correlated with the length of the trans Co–L bond (STE). In agreement with a simple theoretical model, log (KTE) is linearly related to STE for the three S-bonded ligands SO_3^{2-}, RSO_2^-, and $S_2O_3^{2-}$.

Introduction

Over the past few years we have been interested in elucidating the nature of trans effects in octahedral complexes, especially those induced by sulfur bonded to cobalt(III).[1–3,6–8] Coordinated sulfur atoms can exert both a kinetic trans effect (KTE), wherein the ligand situated trans to sulfur is labilized, and a structural trans effect (STE), wherein the ligand situated trans to sulfur has a lengthened Co–ligand bond. We have

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