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The complete thermodynamic cycle of $CoCl_2$–pyridine complex formation

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The formation of $[CoCl_2(py)]$ and $[CoCl_2(py)_2]$ from $CoCl_2$ and pyridine is one of the rare cases where the formation of a complex can be studied in the gas phase and in solution. By measuring the solvation enthalpies of all the partners of the reaction a complete thermodynamic cycle for this complex-formation reaction has been established. It shows that the stabilities of $[CoCl_2(py)]$ and $[CoCl_2(py)_2]$ are much larger in the gas phase than in solution. In cyclohexanone $CoCl_2$ is an uncharged tetrahedral solvent complex $[CoCl_2(solv)_2]$, which upon addition of pyridine forms $[CoCl_2(py)\cdot solv]$ and $[CoCl_2(py)_2]$. In acetonitrile the situation is similar but the electrical conductivity suggests some ionic dissociation. In spite of the different donor atoms the two solvents attenuate the gas-phase stability by almost the same amount; in the gas the enthalpy of formation of $[CoCl_2(py)_2]$ is -231 kJ mol^{-1}, in cyclohexanone -52 kJ mol^{-1} and in acetonitrile -49 kJ mol^{-1}.

Usually, metal complex formation is conceived as the addition of a ligand to a metal cation. In general, such reactions take place in solution and a closer look shows them to be an exchange of solvent molecules by another donor with a reorganisation of the solvation sheath of all reaction partners as a consequence. The only way to distinguish between the two contributions to the metal complex stability, the metal to ligand bond on the one hand and the changes in the solvation energies of the reaction partners on the other, is to study metal complex-formation reactions in the gas phase and in solution. In the gas phase the metal–ligand bond energy is directly accessible by measuring the stability constant. The difference between the complex stabilities in the gas and in solution is due to the different solvation energies of the reaction partners and to the change in solvation energy in the course of the reaction in solution. If, in addition to the stability of the complex in the gas phase, all the solvation energies are measured, a detailed analysis of the energetics of the metal complex reaction becomes possible. Unfortunately, metal complex-formation reactions where such an analysis is possible are rare; most complexes lack the necessary gas-phase stability.

The formation of $[CoCl_2(py)_2]$ (py = pyridine) in organic solvents was reported by Logachev and Doulova[1] in 1971. The solubility in organic solvents indicates that $[CoCl_2(py)_2]$ is a molecular species and that its formation might therefore be studied in the gas phase. This was indeed possible.[2]

The present paper deals with an investigation of the solvation energies of the reaction partners in two solvents, cyclohexanone and acetonitrile, and with the conclusions which can be drawn from the complete thermodynamic cycle of this metal complex-formation reaction.

Experimental

Chemicals

The compounds $[CoCl_2(py)_2]$ and $[CoCl_2(py)]$ were prepared according to ref. 3. Pyridine, acetonitrile and cyclohexanone were Fluka® p.a.

Calorimetric measurements

Dissolution enthalpies were measured in a non-isothermal non-adiabatic calorimeter as described elsewhere.[4] Enthalpometric titrations were performed with a LKB 2277 Thermal Activity Monitor.

Spectrophotometric titrations

Titrations were performed by adding pyridine solution with a 10 μl Hamilton® syringe to a cobalt(II) chloride solution in a thermostatted 1 cm spectrophotometric cell. The absorbance was measured from 500 to 750 nm with a Perkin-Elmer Lambda 2 spectrophotometer. From the data the equilibrium constants, see equations (6) and (7), were obtained as discussed in ref. 2.

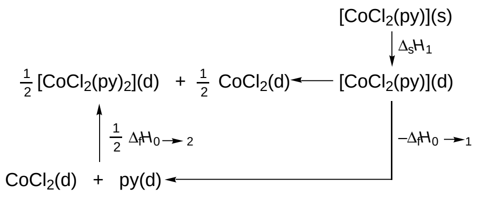
Results

Evaluation of calorimetric measurements

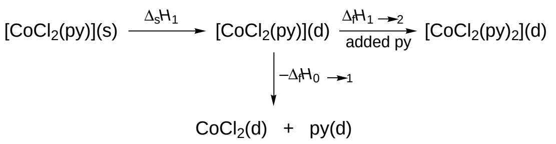
When $[CoCl_2(py)_n](s)$ (n = 0–2) is dissolved there are, in general, two contributions to the observed heat effect: (*i*) the dissolution enthalpy of the compound itself and (*ii*) the enthalpies of all the reactions leading to the equilibrium composition of the solution. To obtain the various dissolution and reaction enthalpies as they appear in the thermodynamic cycles (Schemes 4 and 5), five types of experiments had to be performed. In their presentation J_{meas} is the heat energy (J) determined in the actual calorimetric experiment. Other symbols correspond to those used in the thermodynamic cycles (Schemes 4 and 5) and are defined when introduced for the first time.

Experiment 1. Dissolving $CoCl_2(s)$ in pure solvent, $CoCl_2(s) \xrightarrow{\Delta_sH_0} CoCl_2(d)$, gives $J_{meas} = \text{mol } CoCl_2 \times \Delta_sH_0$.

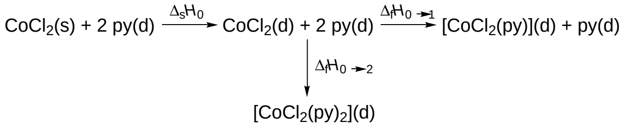
Experiment 2. Dissolving $[CoCl_2(py)](s)$ in pure solvent results in the reactions in Scheme 1. From which equation (1) can be derived.



Scheme 1



Scheme 2



Scheme 3

$$J_{\mathbf{meas}} = \text{mol } [CoCl_2(py)]_{\mathbf{tot}} \times \Delta_s H_1 + \text{mol py}_{\mathbf{free}} \times -\Delta_f H_{0\to1} + \text{mol } [CoCl_2(py)_2] \times (\tfrac{1}{2}\Delta_f H_{0\to2} - \Delta_f H_{0\to1}) = \text{mol } [CoCl_2(py)]_{\mathbf{tot}} \times \Delta_s H_1 - \{\text{mol py}_{\mathbf{free}} + \text{mol } [CoCl_2(py)_2]\} \times \Delta_f H_{0\to1} + \text{mol } [CoCl_2(py)_2] \times \tfrac{1}{2}\Delta_f H_{0\to2} \quad (1)$$

Experiment 3. Dissolving $[CoCl_2(py)](s)$ in solvent containing added pyridine results in the reactions shown in Scheme 2, from which equation (2) is obtained. Adding enough pyridine makes

$$J_{\mathbf{meas}} = \text{mol } [CoCl_2(py)]_{\mathbf{tot}} \times \Delta_s H_1 + \text{mol } [CoCl_2(py)_2](d) \times \Delta_f H_{1\to2} - \text{mol } CoCl_2(d) \times \Delta_f H_{0\to1} \quad (2)$$

the third contribution to $J_{\mathbf{meas}}$ negligible.

Experiment 4. Dissolving $[CoCl_2(py)_2](s)$ in solvent containing added pyridine, $[CoCl_2(py)_2](s) \xrightarrow{\Delta_s H_2} [CoCl_2(py)_2](d) \xrightarrow{-\Delta_f H_{1\to2}} [CoCl_2(py)](d) + py(d)$, results in $J_{\mathbf{meas}} = \text{mol } [CoCl_2(py)_2]_{\mathbf{tot}} \times \Delta_s H_2 + \text{mol } [CoCl_2(py)](d) \times -\Delta_f H_{1\to2}$. Adding enough pyridine makes the second contribution to $J_{\mathbf{meas}}$ negligible.

Experiment 5. Dissolving $CoCl_2(s)$ in solvent containing added pyridine results in the reactions shown in Scheme 3 from which expression (3) is obtained. Adding enough pyridine

$$J_{\mathbf{meas}} = \text{mol } CoCl_{2\mathbf{tot}} \times \Delta_s H_0 + \text{mol } [CoCl_2(py)_2](d) \times \Delta_f H_{0\to2} + \text{mol } [CoCl_2(py)](d) \times \Delta_f H_{0\to1} \quad (3)$$

makes the third contribution to $J_{\mathbf{meas}}$ negligible.

For given concentrations of $[Co]_{\mathbf{tot}}$ and $[py]_{\mathbf{tot}}$ the equations (4)–(7) allows one to calculate for every solution the individual

$$[Co]_{\mathbf{tot}} = [CoCl_2] + [CoCl_2(py)] + [CoCl_2(py)_2] \quad (4)$$

$$[py]_{\mathbf{tot}} = [py] + [CoCl_2(py)] + 2\,[CoCl_2(py)_2] \quad (5)$$

$$K_1 = [CoCl_2(py)]/[CoCl_2][py] \quad (6)$$

$$\beta_2 = [CoCl_2(py)_2]/[CoCl_2][py]^2 \quad (7)$$

equilibrium concentrations and to attribute the total measured heat effects to their formation. Experiments 1–4 yield $\Delta_s H_0$, $\Delta_s H_1$, $\Delta_s H_2$, $\Delta_f H_{0\to1}$, $\Delta_f H_{1\to2}$ (and $\Delta_f H_{0\to2} = \Delta_f H_{0\to1} + \Delta_f H_{1\to2}$); $\Delta_f H_{0\to2}$ is obtained from experiment 5. In addition, $\Delta_f H_{0\to1}$ and $\Delta_f H_{1\to2}$ in cyclohexanone were determined by enthalpometric titration. The results are listed in the thermodynamic cycles, Schemes 4 and 5.

Complex formation in solution

The results of a spectrophotometric titration of $CoCl_2$ with pyridine in cyclohexanone and in acetonitrile are presented in Fig. 1 to illustrate the raw data. The penultimate spectrum showing a maximum absorbance at 610 nm corresponds to a mixture of cobalt : pyridine = 1 : 3. The last spectrum is actually a superposition of two spectra where Co : py = 1 : 18 and 1 : 30. It shows that the formation of $[CoCl_2(py)_n]$ (n = 3 or 4) need not be considered under the conditions employed.

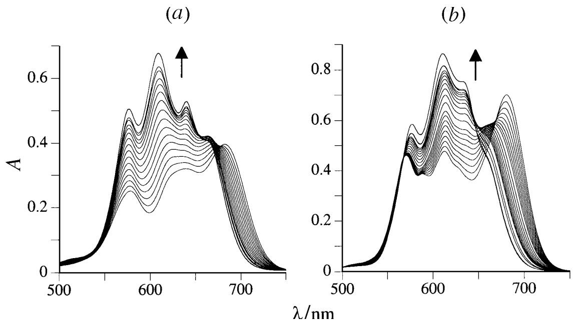


Fig. 1 Spectrophotometric titration of $CoCl_2$ with pyridine in cyclohexanone (*a*) and in acetonitrile (*b*)

Table 1 Formation constants of $[CoCl_2(py)]$ and $[CoCl_2(py)_2]$ in cyclohexanone and acetonitrile

	Cyclohexanone		Acetonitrile	
	This work	Ref. 1	This work	Ref. 1
$K_1 = \frac{[CoCl_2(py)]}{[CoCl_2][py]}$	$10^{4.63}$	—	$10^{3.59}$	—
$K_2 = \frac{[CoCl_2(py)_2]}{[CoCl_2(py)][py]}$	$10^{3.76}$	—	$10^{2.80}$	—
$\beta_2 = \frac{[CoCl_2(py)_2]}{[CoCl_2][py]^2}$	$10^{8.39}$	$10^{5.8}$	$10^{6.39}$	$10^{5.0}$

The evaluation of the data (80 wavelength–absorbance data pairs for each of the 21 spectra) has been discussed in ref. 2. The equilibrium constants (average from four titrations per solvent) are shown in Table 1.

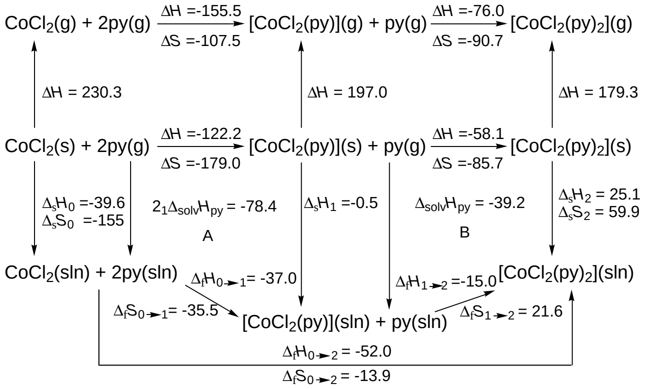
Discussion

Equilibrium constants

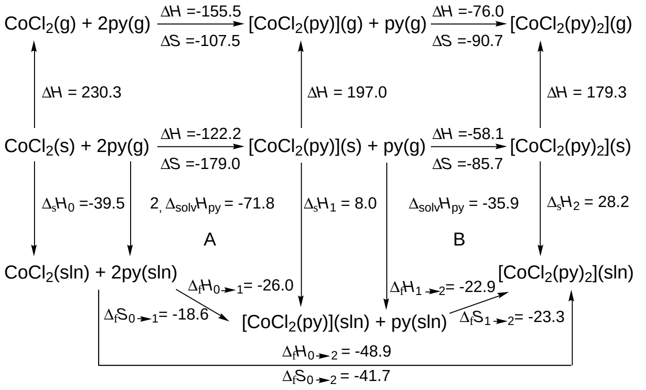
Logachev and Dulova[1] reported the overall formation constants of $[CoCl_2(py)_2]$ in various solvents but not the stepwise formation constants of $[CoCl_2(py)]$ and $[CoCl_2(py)_2]$. Their value for $[CoCl_2(py)_2]$ is smaller than ours (Table 1). The nitrogen of acetonitrile is certainly a better donor for Co^{II} than is the oxygen of cyclohexanone. Consequently more energy is needed to replace acetonitrile by pyridine than to replace cyclohexanone. Therefore the pyridine complexes are less stable in acetonitrile than in cyclohexanone. The spectra used for the spectrophotometric determination of the equilibrium constants show, by the position and intensity of the absorption bands, that solvated $CoCl_2$ as well as $[CoCl_2(py)]$ and $[CoCl_2(py)_2]$ are tetrahedral species. The complexation therefore clearly involves substitution of co-ordinated solvent molecules by pyridine.

Nevertheless there is a difference in the electrical conductivity of the solutions of $CoCl_2$ and $[CoCl_2(py)_2]$ in the two solvents. In cyclohexanone the conductivity of 1.4 mmol dm^{-3} solutions of $CoCl_2$ or $[CoCl_2(py)_2]$ is less than 1 μS cm^{-1} while it is 60 μS cm^{-1} for a 1.6 mmol dm^{-3} solution of $CoCl_2$ in acetonitrile dropping to 45 μS cm^{-1} after addition of an excess of pyridine. The conductivity would therefore indicate that $CoCl_2$ and $[CoCl_2(py)_2]$ are strictly molecular in cyclohexanone, while in acetonitrile, due to its stronger donor property, there is some ionisation.

As mentioned in the Experimental section, the equilibrium constants are crucial for the evaluation of some of the calorimetric measurements.



Scheme 4 Thermodynamic cycle in cyclohexanone; ΔH in kJ mol^{-1}, ΔS in J K^{-1} mol^{-1}



Scheme 5 Thermodynamic cycle in acetonitrile

Calorimetric measurements

In cyclohexanone the values of $\Delta_f H_{0\rightarrow 2}$ from dissolution calorimetry (-51.6 kJ mol^{-1}) and enthalpometric titration (-52.4 kJ mol^{-1}) agree well with that of ref. 1 (-55.7 kJ mol^{-1}). For $\Delta_f H_{0\rightarrow 1}$ and $\Delta_f H_{1\rightarrow 2}$ the enthalpometric titration gave -36.7 and -15.7 kJ mol^{-1} respectively, while dissolution calorimetry gave -38.0 and -14.3 kJ mol^{-1}. The following average values were adopted: $\Delta_f H_{0\rightarrow 1} = -37.0$, $\Delta_f H_{1\rightarrow 2} = -15.0$ kJ mol^{-1}.

In acetonitrile the results of five independent calorimetric determinations of $\Delta_f H_{0\rightarrow 2}$ were between -45.0 and -51.3 kJ mol^{-1} while the temperature dependence of the equilibrium constant of $[CoCl_2(py)_2]$ yielded -53.3 kJ mol^{-1}. The overall average is -49 ± 3 kJ mol^{-1}. This is significantly more negative than the -40.6 kJ mol^{-1} reported in ref. 1. Re-evaluation of the earlier measurements using our data for stepwise complex formation yields -43.7 kJ mol^{-1} for $\Delta_f H_{0\rightarrow 2}$, around 11% less than our value. The van't Hoff plots for the dissolution enthalpy of $[CoCl_2(py)_2]$ in acetonitrile (solubility at 15, 20, 25, 30 and 35 °C) gave 31.4 kJ mol^{-1} in reasonable agreement with the calorimetric determination (28.2 kJ mol^{-1}).

Thermodynamic cycle

The thermodynamic data in solution refer to the standard state of 1 mol dm^{-3} while the standard state of the gas-phase data of ref. 2 is 1 bar (10^5 Pa). In order to compare gas-phase and solution data, the data of ref. 2 have been converted into the 1 mol dm^{-3} standard state. This change affects the enthalpy only slightly but the entropy values much more.

The thermodynamic cycles in Schemes 4 and 5 consist of several subcycles. We first consider the reaction $CoCl_2 + 2\ py \longrightarrow [CoCl_2(py)_2]$. In these schemes this reaction is presented on three levels: in the gas phase, as the reaction of solid $CoCl_2$ with gaseous pyridine and in solution. The sum of the enthalpies involving the gas phase and the solution is 14.4 kJ mol^{-1} in cyclohexanone and 7.6 kJ mol^{-1} in acetonitrile. It is dominated by the large enthalpies of evaporation and of the gas-phase reaction. The observed deviation of the sum from zero is less than the error limit assuming an uncertainty of ±4% for the individual contributions to the sum. Looking at the second and third line of the cycles, the sum of the enthalpies is 15 kJ mol^{-1} in the case of cyclohexanone and 8 kJ mol^{-1} in the case of acetonitrile. This is within the expected limits of error if the enthalpies of the individual steps are uncertain by ±5%.

Table 2 Enthalpies (kJ mol^{-1}) of solvation of reactants and products

	Reactants			Product
Solvent	$CoCl_2$(g)	2 py(g)	Total	$[CoCl_2(py)_2]$(d)
Cyclohexanone	−270	−78	−348	−154
Acetonitrile	−277	−72	−349	−149

Unfortunately the results are not precise enough to consider the subcycles A and B separately. In A the deviation of the enthalpy sum from zero can be reconciled by admitting a ±10% or ±6 kJ mol^{-1} uncertainty of the individual enthalpies but this more favourable situation (as compared to cycle B) may be due to the fact that A is dominated by the large enthalpy of the addition of the first gaseous pyridine to $CoCl_2$(s). In cycle B the sum of the enthalpies deviates by 21 kJ mol^{-1} from the theoretical zero, requiring an uncertainty of over 20% or ±10 kJ mol^{-1} for the individual enthalpies. We consider the thermodynamic values for the reaction in solution rather more reliable than the ones for the formation of solid $[CoCl_2(py)]$ and $[CoCl_2(py)_2]$ from $CoCl_2$(s) and gaseous pyridine. In solution results from various independent methods such as enthalpometric titration, dissolution calorimetry and temperature dependence of the equilibrium constants agree within the uncertainties, while the formation of $[CoCl_2(py)]$(s) and $[CoCl_2(py)_2]$(s) was only determined by a single method: the pyridine pressure when the corresponding complex was decomposed.[2]

The entropy of some of the reactions could not be measured and therefore no check of the zero sum of the entropies of the cycles can be made.

Interpretation

The data from the thermodynamic cycles show that $[CoCl_2(py)]$ and $[CoCl_2(py)_2]$ are much more stable in the gas phase than in solution. The reason is that the reactants have a much higher solvation enthalpy than the products. For $[CoCl_2(py)_2]$ this is brought out by Table 2.

In cyclohexanone and in acetonitrile the dissolution of $CoCl_2$(s) is an exothermic process. The bonding of two solvent molecules to form the complex $[CoCl_2(solv)_2]$(d) largely compensates for the sublimation energy of $CoCl_2$. The enthalpy of solvation of $[CoCl_2(py)_2]$(s) is positive. There are no new bonds formed in the process; the dissolution is entropy driven. The compound $[CoCl_2(py)]$(s) occupies an intermediate position, where the formation of $[CoCl_2(py)(solv)]$(d) makes up for its sublimation energy.

The solid in equilibrium with a saturated solution of $CoCl_2$(s) in acetonitrile is not $CoCl_2$(s) but $[CoCl_2(MeCN)_2]$(s) and therefore the entropy of dissolution of $CoCl_2$ in acetonitrile cannot be derived from solubility measurements. In cyclohexanone the solubility of $CoCl_2$(s) and hence the entropy of dissolution can be determined. It is very negative indicating that the ordering due to the formation of a solvation shell more than compensates for the disorder of the break up of the $CoCl_2$ lattice. The entropy of adding the first and the second pyridine to $CoCl_2$ is similar in the gas phase because the translational entropy is similar for both steps. In solution the entropies of complex formation are much smaller than in the gas because when pyridine binds to cobalt in solution co-ordinated solvent molecules are released to the bulk making the net difference in translational entropy small.

If we assume that the non-zero sum for cycles A and B has to be attributed mainly to the solid–gas reaction and not the solution reaction, the following remarks regarding the complex formation in solution may be made. In acetonitrile the entropies for the first and second addition of pyridine to $CoCl_2$(sln) are similar and negative. This, qualitatively, corresponds to the situation in the gas. In cyclohexanone, however, the entropy of addition of pyridine to $[CoCl_2(py)]$ is largely positive indicating that this process is structure breaking.[5]

A simple model of complex formation[6] assumes that for a given ligand the bond enthalpies are the same and stepwise complex formation is determined by statistics. This definitively is not the case for the formation of $[CoCl_2(py)_2]$ in the gas, while in acetonitrile the enthalpy values for adding the first and second pyridine are rather similar. In both solvents $\log(K_1/K_2)$ is only slightly larger than the statistical value of 0.6. In cyclohexanone the replacement of the first solvent molecule by pyridine is responsible for around two thirds of the enthalpy of formation of $[CoCl_2(py)_2]$; the situation is similar to the one in the gas phase.

Conclusion

While the stability of metal complexes in the gas phase corresponds to the metal–ligand bond energy, in solution the complex-formation energy is attenuated to around 20% of its gas-phase value by the difference in the solvation energies of the reaction partners. There may well be cases where the sequence of stability with different ligands is different in the gas and in solution, similar to the inversion of gas-phase and solution acidity.[7]

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References

1 V. A. Logachev and V. I. Dulova, *Russ. J. Inorg. Chem.* (*Engl. Transl.*), 1971, **16**, 145.
2 C. Daul, F. P. Emmenegger, M. Mlinar and M. Piccand, *Inorg. Chem.*, 1993, **32**, 2992.
3 *Gmelins Handbuch der anorganischen Chemie*, 8. Aufl., Kobalt, Teil B Ergänzungsband, Lieferung 1, Verlag Chemie, Weinheim/Bergstr., 1963, p. 62.
4 H. Piekarski and D. Waliszewski, *Thermochim. Acta*, 1995, **258**, 67.
5 J. Burgess, *Metal Ions in Solution*, Ellis Horwood, Chichester, 1978; *Ions in Solution*, Ellis Horwood, Chichester, 1988.
6 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Interscience, New York, 1988, p. 44.
7 P. Kebarle, *Annu. Rev. Phys. Chem.*, 1977, **28**, 445.

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