

# The Complex of Co(2,2,6,6-tetramethyl-3,5-heptanedionate)<sub>2</sub> with 2,2'-Bipyridine. Its Formation in the Gas Phase and in Solution

Pascal Chassot and Franzpeter Emmenegger\*

Institute of Inorganic and Analytical Chemistry, University of Fribourg,  
Pérolles, CH 1700 Fribourg, Switzerland

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Addition of 2,2'-bipyridine to the red tetrahedral complex Co(tmhd)<sub>2</sub> (tmhd = 2,2,6,6-tetramethyl-3,5-heptanedionate) produces the orange octahedral complex Co(tmhd)<sub>2</sub>bpy. This reaction has been studied by vis spectroscopy from 180 to 370 °C in the gas phase and at 25 °C in cyclohexane and toluene. The high temperature spectra were evaluated by linear programming yielding for the dissociation of Co(tmhd)<sub>2</sub>bpy(g) into Co(tmhd)<sub>2</sub>(g) and bpy(g):  $\Delta_{\text{diss}}H^\circ = 97 \text{ kJ mol}^{-1}$  and  $\Delta_{\text{diss}}S^\circ = 128 \text{ J mol}^{-1} \text{ K}^{-1}$ . The formation of Co(tmhd)<sub>2</sub>bpy in the noncoordinating solvents cyclohexane and toluene was studied by vis spectroscopy and by enthalpometric titration. Within the limits of error the stability of Co(tmhd)<sub>2</sub>bpy is the same in cyclohexane and in toluene:  $\Delta_{\text{assn}}H^\circ = -56 \text{ kJ mol}^{-1}$  and  $\Delta_{\text{assn}}S^\circ = -87 \text{ J mol}^{-1} \text{ K}^{-1}$ . The identical stability in the two solvents is due to an accidental compensation of the different solvation energies of the reaction partners and not to a dominant role of the cobalt–bipyridine bond energy. The enthalpy of solvation of the three equilibrium partners was measured by calorimetry and by the temperature dependence of the solubility. The complete thermodynamic cycle for this ligand addition reaction distinguishes the two contributions to the stability of the complex: the cobalt–bipyridine bond energy (97 kJ mol<sup>-1</sup>) and the solvation energies. The solvation energy of bpy makes the complex more stable in the gas phase than in solution.

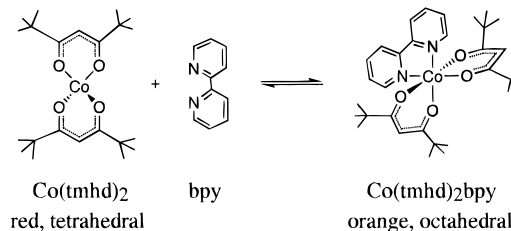
## Introduction

The formation of a complex in solution is, in general, the substitution of coordinated solvent molecules by another ligand. Consequently the solvation of all reaction partners changes. The energy of the metal to ligand bond formation often is of the same order of magnitude as the energy due to the change of solvation.<sup>1</sup> In order to separate the two contributions to the thermodynamic parameters of a complex formation reaction in solution, one has to study the reaction in the gas phase and one has to determine the solvation energies of all the reaction partners. Insufficient thermal stability excludes most systems from being studied in the gas phase. Exceptions are, e.g., the complexes M(AIX<sub>4</sub>)<sub>2</sub>(g) (M = transition metal; X = halogen<sup>2,3</sup> and CoX<sub>2</sub>(py)<sub>n</sub>(g) (X = Cl, Br; n = 1, 2<sup>4,5</sup>).

Many metal diketonates are volatile,<sup>6</sup> and diketonates of divalent cations will often add two additional ligands to reach the coordination number of 6. To study such an addition reaction in the gas phase and in solution it is preferable to choose substituted acetylacetonates to avoid the complications of oligomerization equilibria in solution.<sup>7</sup>

We observed that M(tmhd)<sub>2</sub> (M = Co, Ni; tmhd = 2,2,6,6-tetramethyl-3,5-heptanedionate) adds 2,2'-bipyridine in solution and in the gas phase and therefore we anticipated that these compounds would be suited to investigate the effect of solvation on a complex formation reaction. In addition, for a complete thermodynamic cycle of the reaction the dissolution of all the reaction partners had to be studied. Here we report the addition

## Scheme 1



of bpy to the red tetrahedral Co(tmhd)<sub>2</sub> to form the orange octahedral Co(tmhd)<sub>2</sub>bpy (Scheme 1).

## Experimental Section

(a) **Chemicals.** All chemicals were Fluka p.a. or puriss., except 2,2,6,6-tetramethyl-3,5-heptanedione, which was purum. Solvents were stored over molecular sieves. Co(tmhd)<sub>2</sub> was prepared according to ref 8 and sublimed in vacuum. Co(tmhd)<sub>2</sub>bpy was prepared by mixing 0.01 mol of Co(tmhd)<sub>2</sub> and 0.02 mol of bpy in 100 mL of ethanol:H<sub>2</sub>O = 1:1. After the mixture was stirred for 1 h at 25 °C, the product was collected on a filter and recrystallized from ethanol.

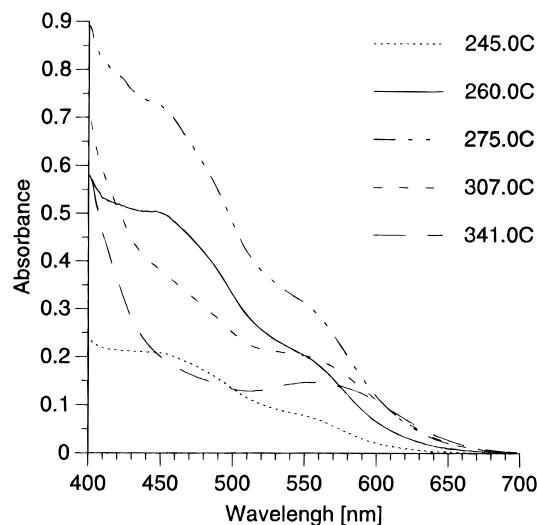
(b) **Thermal Analysis.** DSC and TG were performed on a Mettler TA 3000. The enthalpy of fusion of Co(tmhd)<sub>2</sub>, Co(tmhd)<sub>2</sub>bpy, and bpy was determined by DSC. Modified entrainment<sup>4</sup> was one of the methods used to determine the vapor pressures of Co(tmhd)<sub>2</sub>, Co(tmhd)<sub>2</sub>bpy, and bpy.

(c) **Vis Spectroscopy.** Vis spectroscopy at elevated temperatures was performed with the instrument described in ref 4. From the spectra the equilibrium constant of reaction 1, shown in Figure 2, and the vapor pressures of Co(tmhd)<sub>2</sub> and Co(tmhd)<sub>2</sub>bpy were determined. Vis spectra at ambient temperatures were measured with a Perkin-Elmer Lambda 2 instrument. The equilibrium constant of reaction 2, shown in Figure 2, and temperature dependent solubilities of Co(tmhd)<sub>2</sub>(s) and Co(tmhd)<sub>2</sub>bpy(s) were determined by vis spectroscopy.

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(1) Burgess, J. *Ions in Solution*; Ellis Horwood Ltd.: Chichester, G.B., 1988.  
 (2) Schäfer, H. *Adv. Inorg. Chem. Radiochem.* **1983**, 26, 201.  
 (3) Emmenegger, F. P. *Z. Anorg. Allg. Chem.* **1987**, 545, 56.  
 (4) Emmenegger, F. P.; Piccand M. *Z. Anorg. Allg. Chem.* **1993**, 619, 17.  
 (5) Daul, C.; Emmenegger, F. P.; Mlinar, M.; Piccand, M. *Inorg. Chem.* **1993**, 32, 2992.  
 (6) Winter, C. H. *Strem Chem.* **1994**, 15, 1.  
 (7) Cotton, F. A.; Eiss, R. J. *Am. Chem. Soc.* **1968**, 90, 38.

(8) Hammond, G. S.; Nonhebel, D. C.; Wu, C.-H. *S. Inorg. Chem.* **1963**, 2, 73.



**Figure 1.** How the vis spectrum of a 10 cm ampule with  $[\text{Co}(\text{tmhd})_2] = 3.71 \times 10^{-4} \text{ M}$  and  $[\text{bpy}] = 3.9 \times 10^{-3} \text{ M}$  develops upon heating.

(d) **Calorimetry.** Enthalpies of dissolution were determined by H. Piekarski, University of Lodz, Poland, with a calorimeter described elsewhere.<sup>9</sup> Enthalpometric titrations were performed by N. Ghoneim, University of Fribourg, with a "LKB 2277 Thermal Activity Monitor".

## Results

The  $\Delta H^\circ$  and  $\Delta S^\circ$  values of all the reactions that make up the thermodynamic cycle presented in Figure 2 had to be determined. Some of these reactions have been studied by various methods. In the following presentation the numbers of the reactions correspond to their number in the thermodynamic cycle, Figure 2.

**Reaction 1.**  $\text{Co}(\text{tmhd})_2\text{bpy}$  and excess bpy were sealed in an evacuated spectrophotometric cell that was placed in the furnace of the spectrophotometer. Above 180 °C the spectrum of  $\text{Co}(\text{tmhd})_2\text{bpy}(\text{g})$  was seen; the absorbance increased with temperature until a maximum was reached corresponding approximately to the complete evaporation of the complex. At higher temperatures the absorbance decreased due to reaction 1 and, depending on the amount of excess of bpy present, the spectrum of  $\text{Co}(\text{tmhd})_2(\text{g})$  could be obtained (Figure 1).

Measurements from nine ampules with ratios of  $\text{Co}(\text{tmhd})_2$ :bpy = 1:2.8 to 1:35.5 have been evaluated. The system can be described by four equations containing three dependent variables  $[\text{Co}(\text{tmhd})_2\text{bpy}]$ ,  $[\text{Co}(\text{tmhd})_2]$ ,  $[\text{bpy}]$ , and two independent ones:  $[\text{Co}]_{\text{tot}}$  and  $[\text{bpy}]_{\text{tot}}$ .  $\epsilon_{\text{Co}(\text{tmhd})_2}$  is obtained from the study of reaction 6.

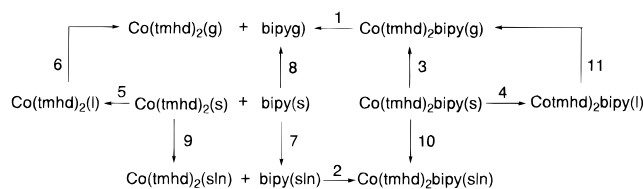
$$A_{\lambda,T} = \epsilon_{\text{Co}(\text{tmhd})_2}[\text{Co}(\text{tmhd})_2] + \epsilon_{\text{Co}(\text{tmhd})_2\text{bpy}}[\text{Co}(\text{tmhd})_2\text{bpy}] \quad (\text{I})$$

$$[\text{Co}]_{\text{tot}} = [\text{Co}(\text{tmhd})_2\text{bpy}] + [\text{Co}(\text{tmhd})_2] \quad (\text{II})$$

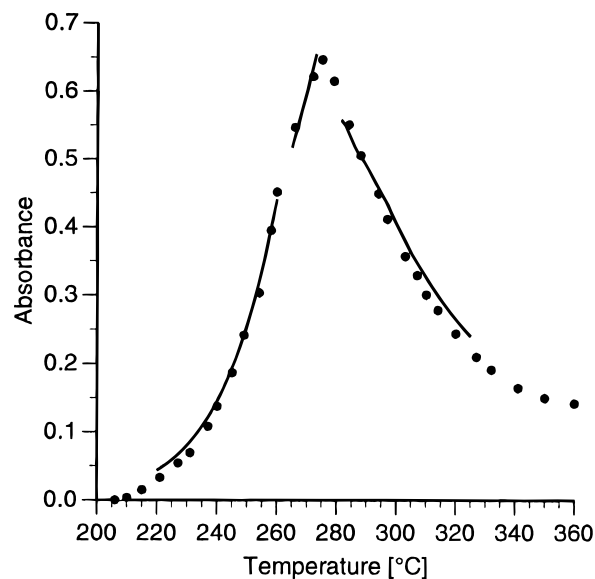
$$[\text{bpy}]_{\text{tot}} = [\text{Co}(\text{tmhd})_2\text{bpy}] + [\text{bpy}] \quad (\text{III})$$

$$K_1 = \frac{[\text{Co}(\text{tmhd})_2][\text{bpy}]}{[\text{Co}(\text{tmhd})_2\text{bpy}]} \quad (\text{IV})$$

$A_{\lambda,T}$  values for the nine samples with different  $[\text{Co}]_{\text{tot}}$  and  $[\text{bpy}]_{\text{tot}}$  values were fitted with a linear programming procedure<sup>5</sup> to give  $K_{\text{diss}}(T)$  and  $\epsilon_{\text{Co}(\text{tmhd})_2\text{bpy}}$ :  $\ln K_{\text{diss}}(T) = f(1/T)$  yields  $\Delta_1 H^\circ = 97 \text{ kJ mol}^{-1}$  and  $\Delta_1 S^\circ = 128 \text{ J mol}^{-1} \text{ K}^{-1}$ .



**Figure 2.** Thermodynamic cycle.



**Figure 3.** How the absorbance at 470 nm in a 10 cm ampule with  $[\text{Co}(\text{tmhd})_2] = 3.71 \times 10^{-4} \text{ M}$  and  $[\text{bpy}] = 3.9 \times 10^{-3} \text{ M}$  develops upon heating. Points are experimental. The lines are calculated using the results of Table 3.

**Table 1.** Thermodynamic Values of the Sublimation of  $\text{Co}(\text{tmhd})_2\text{bpy}$

method	$\Delta_{\text{subl}}H^\circ$ (kJ mol <sup>-1</sup> )	$\Delta_{\text{subl}}S^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> )
vis spectroscopy	130.3	168.1
modified entrainment	124.4	183.1
fusion and evaporation	123	153
average	126	168

This result is used in Figure 3 to retrace  $A_T$  at 470 nm to indicate to what extent the average thermodynamic parameters independently determined for reactions 1, 3, 5, and 6 reproduce the absorbance measured in a specific experiment.

**Reaction 2.** The equilibrium constant  $K_2$  is too large to be determined by vis spectroscopy with great precision. No significant difference of  $K_2$  is observed whether it is determined in the solvents cyclohexane, toluene, benzene, and heptane. The average value is  $\log K_2 = 5.63$  while the average of the enthalpometric titration in benzene and in toluene is  $\log K_2 = 4.85$ . An overall average of  $\Delta_2 G^\circ = 30 \pm 3 \text{ kJ mol}^{-1}$  is adopted. From the enthalpometric titration in benzene and toluene  $\Delta_2 H^\circ = -56 \text{ kJ mol}^{-1}$ ; this yields  $\Delta_2 S^\circ = -87 \text{ J mol}^{-1} \text{ K}^{-1}$ .

**Reaction 3.** When there is an excess of bpy in the ampule the dissociation of  $\text{Co}(\text{tmhd})_2\text{bpy}(\text{g})$  according to reaction 1 is negligible at lower temperatures and it is straightforward to use Beer's law to calculate  $[\text{Co}(\text{tmhd})_2\text{bpy}](\text{g})$  from the absorbance  $A$  and  $\epsilon_{\text{Co}(\text{tmhd})_2\text{bpy}}$  (obtained in the study of reaction 1).

At higher temperatures, when dissociation according to reaction 1 becomes important the composition of the gas phase has to be calculated from  $A_{\lambda,T}$  using eqs I and IV as well as  $\epsilon_{\text{Co}(\text{tmhd})_2\text{bpy}}$  and  $\epsilon_{\text{Co}(\text{tmhd})_2}$ .

The sublimation of  $\text{Co}(\text{tmhd})_2\text{bpy}$  was also studied by "modified entrainment".<sup>4</sup> In addition, the enthalpy and entropy

**Table 2.** Enthalpy and Entropy of Dissolution of Co(tmhd)<sub>2</sub> and Co(tmhd)<sub>2</sub>bpy

method	solvent	Co(tmhd) <sub>2</sub>		Co(tmhd) <sub>2</sub> bpy	
		$\Delta_{\text{sol}}H^\circ$ (kJ mol <sup>-1</sup> )	$\Delta_{\text{sol}}S^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$\Delta_{\text{sol}}H^\circ$ (kJ mol <sup>-1</sup> )	$\Delta_{\text{sol}}S^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> )
calorimetry	cyclohexane	13.4	40.2 <sup>a</sup>	34	57.7 <sup>a</sup>
solubility	cyclohexane	15.2	46.6	33.1	54.8
calorimetry	toluene	15.3	47 <sup>a</sup>	25.5	48 <sup>a</sup>
solubility	toluene			27	53

<sup>a</sup> Entropy values calculated from  $\Delta_{\text{sol}}G^\circ_{298}$  (solubility) and  $\Delta_{\text{sol}}H^\circ_{298}$  (calorimetry).

**Table 3.** Data for the Thermodynamic Cycle of Figure 2

no.	reaction	$\Delta H^\circ$ (kJ mol <sup>-1</sup> )	$\Delta S^\circ$ (kJ mol <sup>-1</sup> K <sup>-1</sup> )	$\Delta G^\circ_{298}$ (kJ mol <sup>-1</sup> )
1	dissociation	97(5)	128(8)	59(7)
2	association	-56(3)	-87(3)	-30(3)
3	sublimation of Co(tmhd) <sub>2</sub> bpy	126(4)	168(15)	76(8)
4	melting of Co(tmhd) <sub>2</sub> bpy	50(4)	92(4)	23(5)
5	fusion of Co(tmhd) <sub>2</sub>	32(2)	76(2)	9(2)
6	evaporation of Co(tmhd) <sub>2</sub>	72(4)	93(5)	44(6)
7	dissolution of bpy			
	(a) cyclohexane	28(1)	91(7)	1(1)
	(b) toluene	19(1)	72(7)	-2(1)
8	sublimation of bpy	75(5)	128(10)	37(8)
9	dissolution of Co(tmhd) <sub>2</sub>			
	(a) cyclohexane	14(1)	43(7)	1(1)
	(b) toluene	15(1)	47(7)	1(1)
10	dissolution of Co(tmhd) <sub>2</sub> bpy			
	(a) cyclohexane	34(1)	56(7)	17(1)
	(b) toluene	26(1)	50(7)	11(1)
11	evaporation of Co(tmhd) <sub>2</sub> bpy	75(3)	73(16)	53(7)
	sum			
	(a) cyclohexane	4	10	0
	(b) toluene	4	19	3

<sup>a</sup> Standard state: 1 mol dm<sup>-3</sup>.

of sublimation correspond to the sum of the corresponding values of fusion (reaction 4) and evaporation (reaction 11) discussed below. Table 1 summarizes the results obtained by the three different methods.

**Reactions 4 and 5.** The temperature and the enthalpy of fusion of Co(tmhd)<sub>2</sub> and Co(tmhd)<sub>2</sub>bpy were determined by DSC. For Co(tmhd)<sub>2</sub>:  $T_{\text{fus}} = 149$  °C,  $\Delta_{\text{fus}}H^\circ = 32$  kJ mol<sup>-1</sup>, and  $\Delta_{\text{fus}}S^\circ = 76$  J mol<sup>-1</sup> K<sup>-1</sup>; for Co(tmhd)<sub>2</sub>bpy:  $T_{\text{fus}} = 272$  °C,  $\Delta_{\text{fus}}H^\circ = 50$  kJ mol<sup>-1</sup>, and  $\Delta_{\text{fus}}S^\circ = 92$  J mol<sup>-1</sup> K<sup>-1</sup>.

**Reaction 6.** The enthalpy and entropy of evaporation of Co(tmhd)<sub>2</sub> were determined by vis spectroscopy and by modified entrainment.<sup>4</sup> The results obtained by the two methods agreed within 3%:  $\Delta_{\text{evap}}H^\circ = 72$  kJ mol<sup>-1</sup> and  $\Delta_{\text{evap}}S^\circ = 93$  J mol<sup>-1</sup> K<sup>-1</sup>.

**Reaction 7.** Calorimetry was used to determine the enthalpy of dissolution of bpy in cyclohexane:  $\Delta_{\text{sol}}H^\circ = 27.6$  kJ mol<sup>-1</sup> and in toluene:  $\Delta_{\text{sol}}H^\circ = 19$  kJ mol<sup>-1</sup>. The solubility in these solvents gives  $\Delta_{\text{sol}}G^\circ$ , from which  $\Delta_{\text{sol}}S^\circ$  is calculated using the calorimetric  $\Delta_{\text{sol}}H^\circ$  value. In cyclohexane,  $\Delta_{\text{sol}}S^\circ = 91$  J mol<sup>-1</sup> K<sup>-1</sup> and in toluene,  $\Delta_{\text{sol}}S^\circ = 72$  J mol<sup>-1</sup> K<sup>-1</sup>.

**Reaction 8.** The vapor pressure of bpy has been determined by modified entrainment,  $\Delta_{\text{evap}}H^\circ = 61.6$  kJ mol<sup>-1</sup> and  $\Delta_{\text{evap}}S^\circ = 122$  J mol<sup>-1</sup> K<sup>-1</sup>, and by IR spectroscopy,<sup>10</sup>  $\Delta_{\text{evap}}H^\circ = 54.2$  kJ mol<sup>-1</sup> and  $\Delta_{\text{evap}}S^\circ = 93.7$  J mol<sup>-1</sup> K<sup>-1</sup> (standard state 1 bar). In general, the enthalpy obtained from a van't Hoff plot is more reliable than the entropy. We therefore use the average enthalpy of evaporation, 57.9 kJ mol<sup>-1</sup>, and the boiling point, 547 K, to calculate the entropy of evaporation:  $\Delta_{\text{evap}}S^\circ = 105.9$  J mol<sup>-1</sup> K<sup>-1</sup>. The melting point of bpy is 72 °C. The enthalpy of melting determined by DSC is 20.5 kJ mol<sup>-1</sup> from which  $\Delta_{\text{melt}}S^\circ = 59.4$  J mol<sup>-1</sup> K<sup>-1</sup>. For the sublimation it follows that  $\Delta_{\text{subl}}H^\circ = 78.4$  kJ mol<sup>-1</sup> and  $\Delta_{\text{subl}}S^\circ = 165.3$  J mol<sup>-1</sup> K<sup>-1</sup>.

In order to be compatible with the other values of the thermodynamic cycle these values have to be converted to the

standard state 1 M:  $\Delta_{\text{subl}}H^\circ = 75$  kJ mol<sup>-1</sup> and  $\Delta_{\text{subl}}S^\circ = 128$  J mol<sup>-1</sup> K<sup>-1</sup>.

**Reactions 9 and 10.** The enthalpy and entropy of dissolution of Co(tmhd)<sub>2</sub> and Co(tmhd)<sub>2</sub>bpy in toluene and cyclohexane were measured by the temperature dependence of the solubility. In addition (and more reliably) the enthalpy of dissolution was determined by calorimetry, which, using  $\Delta_{\text{sol}}G^\circ$  from the solubility measurement, gave an additional value for the entropy of dissolution. These results are presented in Table 2.

The values used in the thermodynamic cycle are as follows: Co(tmhd)<sub>2</sub> in cyclohexane,  $\Delta_{\text{sol}}H^\circ = 14$  kJ mol<sup>-1</sup>,  $\Delta_{\text{sol}}S^\circ = 43$  J mol<sup>-1</sup> K<sup>-1</sup>; Co(tmhd)<sub>2</sub> in toluene,  $\Delta_{\text{sol}}H^\circ = 15$  kJ mol<sup>-1</sup>,  $\Delta_{\text{sol}}S^\circ = 47$  J mol<sup>-1</sup> K<sup>-1</sup>; Co(tmhd)<sub>2</sub>bpy in cyclohexane,  $\Delta_{\text{sol}}H^\circ = 34$  kJ mol<sup>-1</sup>,  $\Delta_{\text{sol}}S^\circ = 56$  J mol<sup>-1</sup> K<sup>-1</sup>; Co(tmhd)<sub>2</sub>bpy in toluene,  $\Delta_{\text{sol}}H^\circ = 26$  kJ mol<sup>-1</sup>,  $\Delta_{\text{sol}}S^\circ = 50$  J mol<sup>-1</sup> K<sup>-1</sup>.

**Reaction 11.** The determination of the vapor pressure of Co(tmhd)<sub>2</sub>bpy(l) by vis spectroscopy is limited to the narrow temperature range between fusion and decomposition of the complex according to reaction 1. A van't Hoff plot of five suitable samples yields  $\Delta_{\text{evap}}H^\circ = 73.3$  kJ mol<sup>-1</sup> and  $\Delta_{\text{evap}}S^\circ = 60.8$  J mol<sup>-1</sup> K<sup>-1</sup>. It is preferable to calculate the enthalpy and entropy of reaction 11 from the data of sublimation (Table 1) and fusion (reaction 4) yielding  $\Delta_{\text{evap}}H^\circ = 77$  kJ mol<sup>-1</sup> and  $\Delta_{\text{evap}}S^\circ = 84$  J mol<sup>-1</sup> K<sup>-1</sup>.

## Discussion

Table 3 summarizes the thermodynamic parameters of all the reactions of the cycle. They all refer to the standard state 1 mol dm<sup>-3</sup>.

When going around a thermodynamic cycle the sum of the enthalpies and entropies should obviously be zero. In the present example it is very difficult to estimate the determinate error of the individual thermodynamic values of the cycle because systematic errors can neither be excluded nor reliably

estimated. The error limits given in Table 3 for a particular reaction are standard deviations of a series of measurements, often performed with several independent methods. If one applies the rule of error propagation,<sup>9</sup> the sum of the enthalpies, entropies, and free energies should be  $0 \pm 10 \text{ kJ mol}^{-1}$ ,  $0 \pm 24 \text{ J mol}^{-1} \text{ K}^{-1}$ , and  $0 \pm 15 \text{ kJ mol}^{-1}$  respectively. The experimental results given in the last two rows of Table 3 are well within these limits of error. This internal consistency of the data is certainly an indication of their validity.

On one hand the results illustrate some general concepts of metal complex formation. On the other hand they show that for metal complex formation in solution the energy related to solvation is of the same order of magnitude as the metal to ligand bond energy.

We would like to emphasize the following points.

(1) In the gas, the enthalpy of the formation of  $\text{Co}(\text{tmhd})_2\text{bpy}$  corresponds to the bond energy of  $\text{Co}-\text{bpy}$ . The enthalpies of solvation of both complexes,  $\text{Co}(\text{tmhd})_2$  and  $\text{Co}(\text{tmhd})_2\text{bpy}$ , are two-thirds of the enthalpy of complex formation in the gas phase, illustrating the importance of solvation in metal complex formation reactions.  $\Delta_{\text{form}}H^\circ$  of the complex in solution is only 44% of the  $\text{Co}-\text{bpy}$  bond energy, the remaining 56% of is spent to "desolvate" the bpy when it moves from the bulk into the coordination sphere.

(2)  $\Delta G^\circ$  of the complex formation is  $29 \text{ kJ mol}^{-1}$  more negative in the gas phase than in cyclohexane. The lower stability in solution than in the gas phase is due to the more negative  $\Delta_{\text{solv}}G^\circ$  of the reactants than of the product.  $\Delta_{\text{solv}}G^\circ$

values for  $\text{Co}(\text{tmhd})_2(\text{g})$  and for  $\text{Co}(\text{tmhd})_2\text{bpy}(\text{g})$  are similar, but  $\Delta_{\text{solv}}G^\circ$  of bipyridine adds to the  $\Delta_{\text{solv}}G^\circ$  of the reactants.

(3) As one would expect, the entropy of complex formation in the gas is more negative than in solution because in solution the loss of translational entropy due to the association of two freely moving molecules is partially compensated for by the release of solvent molecules out of the solvation shell (of bpy) into the bulk.

(4) Within the limits of error the stability of  $\text{Co}(\text{tmhd})_2\text{bpy}$  is the same in toluene and in cyclohexane. But the solvation enthalpy of bipyridine is  $9 \text{ kJ mol}^{-1}$  more negative in toluene than in cyclohexane. Almost the same difference is shown by  $\text{Co}(\text{tmhd})_2\text{bpy}$ , namely  $8 \text{ kJ mol}^{-1}$ . This suggests a bonding interaction of the  $\pi$ -electron system of toluene with bipyridine. If one compares the addition of bipyridine to  $\text{Co}(\text{tmhd})_2$  in the two solvents, the difference of the solvation energy of the reactant bipyridine is compensated by the difference of the solvation energy of the product  $\text{Co}(\text{tmhd})_2\text{bpy}$ . The result is equal stability of  $\text{Co}(\text{tmhd})_2\text{bpy}$  in the two solvents, but contrary to what one might expect this is not due to the dominating cobalt–bipyridine bond energy but to an accidental compensation of differences in solvation energies.

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(10) Asmis, K. Diploma thesis, University of Fribourg, 1992.

(11) Skoog, D. A.; West, D. M. *Fundamentals of Analytical Chemistry*; Holt, Rinehart and Winston Inc.: New York, 1963.