

A 1,10-Phenanthroline Adduct Complex of Bis(*N,N*-diethyldithiocarbamato)nickel(II)

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The first example of the addition of a chelating diamine to square-planar bis(dithiocarbamato)nickel(II), forming an octahedral complex, is reported. The equilibrium constant of the reaction bis(*N,N*-diethyldithiocarbamato)nickel(II) (abbreviated Ni(dtc)₂) + *o*-phenanthroline (abbreviated phen) = Ni(dtc)₂phen has been determined spectrophotometrically from 293 to 313 K in toluene, acetone, and chloroform to get the enthalpy and entropy of the reaction in these three solvents. The higher stability in toluene ($K_{298} = 2237 \text{ M}^{-1}$) as compared to that in chloroform ($K_{298} = 96 \text{ M}^{-1}$) is mainly due to a more negative enthalpy of reaction in toluene ($-49.7 \text{ kJ mol}^{-1}$ in toluene vs $-40.1 \text{ kJ mol}^{-1}$ in chloroform), while the higher stability in acetone ($K_{298} = 1126 \text{ M}^{-1}$) as compared to that in chloroform is mainly due to a less negative entropy of reaction ($-64.5 \text{ J K}^{-1} \text{ mol}^{-1}$ in acetone vs $-96.2 \text{ J K}^{-1} \text{ mol}^{-1}$ in chloroform). By two independent thermodynamic cycles ΔH , ΔS , and ΔG of the above reaction in the solid state have been evaluated. The main difference between the solution and the solid-state reaction is the much less negative entropy of the latter. The rate of formation of Ni(dtc)₂phen has been investigated by stopped flow. It is second order, and the rate constants are proportional to the stability constants of the complex in the respective solvent. The rate of decomposition is first order and shows no solvent dependence. The energy of the "desolvation" of the reactants in the course of forming the reaction intermediate has been correlated to the activation energy of the formation of Ni(dtc)₂phen.

Introduction

Xanthates (ROCS₂⁻),¹ dithiophosphates ((RO)₂PS₂⁻),² and dithiocarbamates (R₂NCS₂⁻)¹ form planar, diamagnetic nickel(II) complexes containing a NiS₄ unit. With amines these nickel complexes form octahedral addition compounds. The kinetics of the formation and the stability of such amine addition complexes of nickel xanthates^{3,5} and nickel dithiophosphates⁴ have been extensively studied, but surprisingly little is known about the corresponding amine addition to nickel dithiocarbamates.⁶ Considering the widespread interest in metal dithiocarbamate complexes⁷ on one hand and in the mechanism of additions to square-planar nickel complexes⁸ on the other hand, it seemed worthwhile to fill this gap.

The addition of a bidentate amine such as *o*-phenanthroline to nickel dithiocarbamate involves the moving of the dithiocarbamate from its position in the plane to an edge of the octahedron (Figure 1). This octahedral complex resembles the intermediate of the substitution reaction of square-planar complexes and, in this perspective, merits additional interest. In order to elucidate the role of solvation, the rate of formation and the stability of Ni(dtc)₂phen were determined in the three solvents toluene, acetone, and chloroform at various temperatures each.

Abbreviations

Ni(dtc)₂: bis(*N,N*-diethyldithiocarbamato)nickel(II)Ni(xan)₂: bis(*O*-ethyl xanthato)nickel(II)Ni(dtp)₂: bis(*O,O*-diethyl phosphorodithioato-*S,S'*)nickel(II)Ni(Sacac)₂: bis(4-mercaptopent-3-en-2-onato)nickel(II) = bis(thioacetylacetonato)nickel(II)phen: 1,10-phenanthroline (*o*-phenanthroline)

pic: 4-methylpyridine

Ni(dtc)₂phen: bis(*N,N*-diethyldithiocarbamato)nickel(II)-1,10-phenanthroline

Experimental Section

Chemicals. All solvents were from Merck (pro analysi). They were used without further purification. *o*-Phenanthroline was from Fluka (purissimum) and was dried under vacuum at 70 °C. Bis(diethyldithiocarbamato)nickel(II) (=Ni(dtc)₂) was prepared by mixing equimolar amounts of aqueous solutions of nickel chloride and sodium dithiocarbamate (Fluka, purum). The precipitate was washed, dried, and dissolved in acetone. After filtration the acetone solution was cooled in the refrigerator. Dark green needles of Ni(dtc)₂ were obtained and dried under vacuum at 70 °C. Ni(dtc)₂phen was prepared by dissolving 2 mmol of Ni(dtc)₂ and 2–6 mmol of phenanthroline in acetone at around 50 °C and slowly cooling the saturated solution. Anal. Calcd for NiC₂₂H₂₈N₄S₄: C, 49.30; H, 5.23; N, 10.45. Found: C, 49.12; H, 5.24; N, 10.31.

Equilibrium Constants. To 3 mL of Ni(dtc)₂ solutions (2–5 mM) in 1-cm spectrophotometric cells were added concentrated phenanthroline solution (0.255 M) or weighted portions of solid phenanthroline. Spectra were recorded with a Perkin-Elmer Lambda-5 spectrophotometer. Extinction coefficients and equilibrium constants were evaluated simultaneously by a computer program.⁹ To measure the temperature dependence of the equilibrium constants from 293 to 313 K in 5 K steps, a thermostated cell holder and magnetic stirring within the optical cell were employed. The temperature in the solution was measured with a copper/constantan thermocouple.

Kinetic Measurements. The formation of Ni(dtc)₂phen was measured with a HI-TECH-SFA11 stopped-flow spectrophotometer at 600 nm. The trace of the photomultiplier output was displayed on a storage oscilloscope (Gould OS 4020) and simultaneously transferred to a computer to evaluate the pseudo-first-order rate constant (k_{obs}).

Measurements at Elevated Temperature. Gas-phase spectra at elevated temperature were measured with a modified Zeiss PMQ2 spectrophotometer described elsewhere.¹⁰ The melting points of Ni(dtc)₂ and Ni(dtc)₂phen and the enthalpy of melting of *o*-phenanthroline were determined by DSC on a Mettler TA 3000 instrument.

Solubility Measurements. The solubilities of Ni(dtc)₂ and Ni(dtc)₂phen in toluene, acetone, and chloroform were determined spectrophotometrically between 273 and 303 K in 5 K steps. For Ni(dtc)₂phen, to prevent dissociation of the complex, the solvents were phenanthroline solutions, i.e. 0.01, 0.015, and 0.025 M phenanthroline in toluene, 0.0225, 0.03, and 0.0375 M phenanthroline in acetone, and 0.75 M phenanthroline in chloroform. No systematic influence of the phenanthroline concentration on the solubility of Ni(dtc)₂phen was detected. In chloroform all concentrations are large and appreciable deviation from "ideal" behavior is expected.

The solubility of *o*-phenanthroline was determined by equilibrating known amounts of solid and solvent. The undissolved residue as well as the solid recovered after evaporation of an aliquot of the solution were weighted. The enthalpy of solvation of *o*-phenanthroline in the three solvents was determined with a LKB 8700 calorimeter.

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- (8) Elias, H.; Hess, D.; Schumann, M.; Zang, V. *Book of Abstracts*; 24th International Conference on Coordination Chemistry, Athens, 1986; Chimika Chronika/New Series: Athens; p 58.

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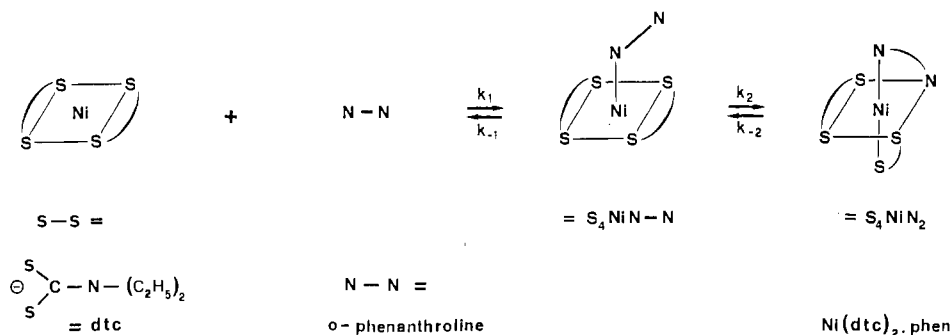


Figure 1. Reaction scheme for the addition of *o*-phenanthroline to bis(dithiocarbamato)nickel(II).

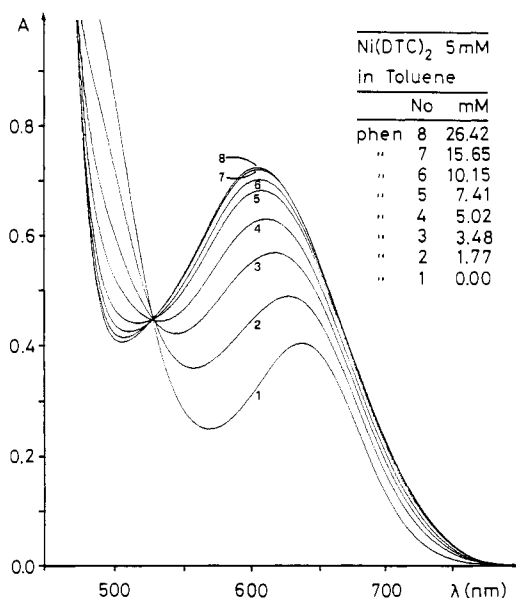


Figure 2. Spectral changes in the course of phenanthroline addition to Ni(dtc)₂ in toluene at 298 K.

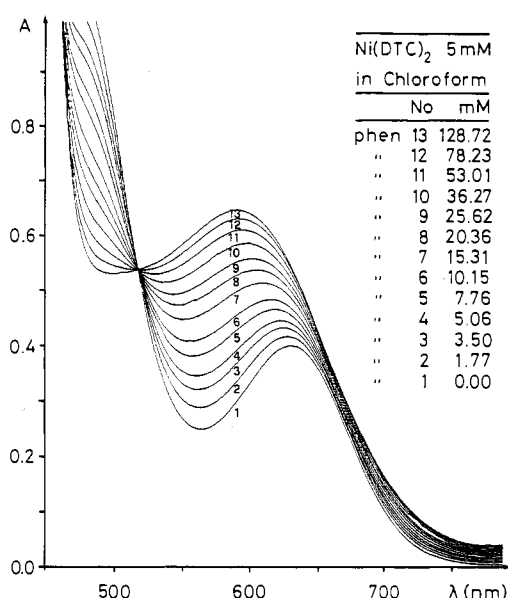
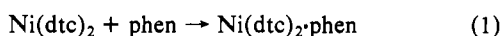


Figure 3. Spectral changes in the course of phenanthroline addition to Ni(dtc)₂ in chloroform at 298 K.

Results

Spectrophotometric Equilibrium Measurements. The change of the intensity and position of the absorption band around 600 nm after addition of phen to Ni(dtc)₂ is shown in Figure 2 for the solvent toluene and in Figure 3 for the solvent chloroform. The two figures illustrate the lower stability of the Ni(dtc)₂phen adduct in chloroform because in chloroform much higher phenanthroline concentrations than in toluene produce smaller spectral changes. In acetone the situation is intermediate between those in toluene and chloroform. *K* values for reaction 1 as derived from



these spectrophotometric measurements are listed in Table IV. In all three solvents the isosbestic point is lost at high phenanthroline concentration. The species responsible for this has not been investigated.

The temperature dependence of the equilibrium constants with the assumption of temperature-independent extinction coefficients yielded the "second-law" values²² of the enthalpy and entropy presented in the (5) column of Table II.

Kinetic Measurements. The results of the kinetic measurements are presented in Figure 4. Plots of k_{obs} against ligand concentration are linear, with zero intercept, over a 4–6-fold change in ligand concentration. The formation of Ni(dtc)₂phen is therefore second order, and the so-called "solvent path"¹¹ is not important. The second-order rate constant $k_{2\text{nd}}$ is related to k_{obs} by $k_{2\text{nd}} = k_{\text{obs}}/[\text{phen}]_{\text{av}}$, where $[\text{phen}]_{\text{av}} = [\text{phen}]_{\text{init}} - [\text{Ni}]/2$. Activation parameters derived from the temperature dependence of $k_{2\text{nd}}$ are listed in Table V.

Vapor Pressure Measurements. When Beer's and van't Hoff's laws are combined, eq 2 is obtained,²¹ which is used to determine ΔH° and ΔS° of the evaporation from the measurement of the optical absorbance of the equilibrium vapor of a condensed phase as a function of the inverse temperature. *o*-Phenanthroline has

$$\ln(AT) = \frac{-\Delta H^\circ_{\text{evap}}}{RT} + \frac{\Delta S^\circ_{\text{evap}}}{R} + \ln\left(\frac{\epsilon d}{R}\right) \quad (2)$$

d = optical path length

an optical absorption band around 260 nm. In agreement with reported values,¹² we find $\epsilon = 29\,300 \text{ M}^{-1} \text{ cm}^{-1}$ at 264 nm in chloroform and we assume this value to be valid in the gas phase also. The optical absorption of the gas phase in equilibrium with *o*-phen(liq) was measured in a 1-cm and in a 10-cm cell from 120 to 200 °C. The absorption values of the 10-cm cell (120–160 °C) were divided by 10 and, together with the absorption of the 1-cm cell (160–200 °C), they were used for the $\ln(AT) = f(1/T)$ plot of Figure 5. From this plot $\Delta H^\circ_{\text{evap}} = 88.7 \pm 5 \text{ kJ mol}^{-1}$ and $\Delta S^\circ_{\text{evap}} = 178.5 \pm 10 \text{ J K}^{-1} \text{ mol}^{-1}$ were computed by using eq 2. Entropy values from the temperature dependence of equilibrium constants, so-called "second law" values, are known to be often rather unprecise,²² and therefore the Trouton-law value of $\Delta S^\circ_{\text{evap}} \approx 100 \text{ J K}^{-1} \text{ mol}^{-1}$ for the evaporation of phenanthroline is to be preferred. This yields $\Delta H^\circ_{\text{evap}} = 54.7 \text{ kJ mol}^{-1}$.

The melting point and the enthalpy of melting of *o*-phenanthroline have been determined by DSC: mp 118.3 °C, $\Delta H^\circ_{\text{melt}} = 15.1 \pm 0.2 \text{ kJ mol}^{-1}$. From these values $\Delta S^\circ_{\text{melt}} = 38.6 \pm 0.5 \text{ J K}^{-1} \text{ mol}^{-1}$. This allows us to calculate the enthalpy and entropy of sublimation of *o*-phenanthroline (Table III).

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Table I. Stability of Amine Adducts of Nickel Complexes in Benzene or Toluene

Ni complex	amine	log β_2 , M ⁻²	ΔH , kJ mol ⁻¹	ΔS , J K ⁻¹ mol ⁻¹	ref	amine	log K	ΔH , kJ mol ⁻¹	ΔS , J K ⁻¹ mol ⁻¹	ref
Ni(S ₂ COEt) ₂	py	3.44	-75	-186	19	bpy	6.20			3
Ni(S ₂ P(OEt) ₂) ₂	py	3.34	-70	-172	18, 20	bpy	6.43	-76	-121	4
Ni(S ₂ P(OEt) ₂) ₂	4-pic	3.86	-76	-189	5, 19	phen	ca. 9			4
Ni(Sacac) ₂ ^a	4-pic	-0.38			5	phen	4.43	-62	-123	5
Ni(S ₂ CN(Et) ₂) ₂	py	-1.06	-28	-114	17	phen	3.35	-50	-101	this work

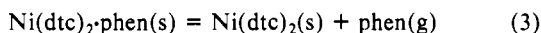
^aSacac = thioacetylacetonate (4-mercaptopent-3-en-2-one).

Table II. ΔH° , ΔS° , and ΔG° for the Reactions of the Born-Haber Cycle of Scheme I

solvent	ΔH°_{298} , kJ mol ⁻¹				
	⑤	④	③	②	① ^b
toluene	-49.7	17.4	14.8	23.9	-28.4 ± 6
acetone	-36.6	28.0	12.5	27.9	-24.2 ± 8
chloroform	-40.1	15.5	-7.5	13.4	-49.7 ± 5
solvent	ΔS°_{298} , J K ⁻¹ mol ⁻¹				
	⑤	④	③	②	① ^b
toluene	-101.0	17.3	30.1	36.2	-52.0 ± 17
acetone	-64.5	56.2	40.6	52.7	-27.4 ± 16
chloroform	-96.2	37.1		24.1	
solvent	ΔG°_{298} , kJ mol ⁻¹				
	⑤	④	③	②	① ^b
toluene	-19.1	12.2	5.8	13.1	-12.4 ± 1.4
acetone	-17.4	11.3	0.5	12.2	-9.1 ± 1.2
chloroform	-11.3	4.4	<0.5	6.2	<-8.5

^aError limits: For ②, ③, ④, and ⑤ the errors in ΔG°_{298} are estimated to be around ±5%, for ΔH°_{298} around ±10%, and for ΔS°_{298} around ±15%. ^bCalculated ① = ⑤ - ④ + ③ + ②.

The melting points of Ni(dtc)₂ and Ni(dtc)₂·phen are 234 and 213 °C, respectively. They were determined by DSC. The phenanthroline pressure in equilibrium with Ni(dtc)₂·phen at 156–196 °C therefore corresponds to the equilibrium constant of reaction 3. The optical absorption due to phen(g) was mea-



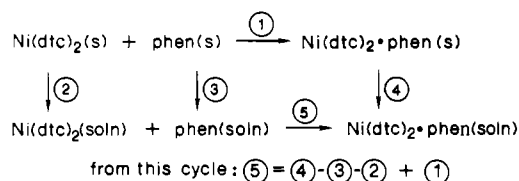
sured for two Ni(dtc)₂·phen samples in 10-cm optical cells. By thermal cycling between 174 and 191 °C it was verified that the reaction was reversible. A plot according to eq 2, shown in Figure 5, yielded $\Delta H^\circ(3) = 106.2 \pm 5$ kJ mol⁻¹ and $\Delta S^\circ(3) = 173.5 \pm 10$ J K⁻¹ mol⁻¹. It is reasonable that enthalpy and entropy of reaction 3 are more positive than the values corresponding to the evaporation of phen(l). Figure 5 illustrates that, at a given temperature, the phenanthroline vapor pressure of solid Ni(dtc)₂·phen is indeed smaller than that of molten phenanthroline.

The thermodynamic values of this paragraph are listed in Table III.

Solubility Measurements. The temperature dependence of the solubility of Ni(dtc)₂ and Ni(dtc)₂·phen in toluene, acetone and chloroform yielded the enthalpies and entropies listed in the ② and ④ columns of Table II. The concentrations of the saturated solutions of *o*-phenanthroline in toluene and acetone at 298 K are used to calculate ΔG° of the dissolving reaction, and with the calorimetrically determined enthalpies of solution, the entropies of solution have been computed. The results are listed in the ③ column of Table II. For the chloroform solution of phenanthroline, only a lower limit of the solubility can be given (0.8 M at 298 K) because the solid that precipitates from a saturated solution at 298 K (=0.83 M) is not phenanthroline but phen·CHCl₃. Therefore, our data do not allow us to calculate the entropy of solution of *o*-phenanthroline in chloroform.

Discussion

Stability of Amine Adduct Complexes of Square-Planar Nickel(II) Complexes with Sulfur Donors. The relative stabilities of the pyridine and 4-picoline complexes (Table I) indicate that the Lewis acidity of the nickel is similar in the nickel xanthate and dithiophosphate complexes while it is substantially lower in the

Scheme I

thioacetylacetonate and dithiocarbamate complexes. The same trend is observed in the stabilities of the 2,2'-bipyridyl and 1,10-phenanthroline adducts, but their formation constant is 10³–10⁵ times larger than that of the pyridine adducts. The high stabilities of the phen and bpy adducts are somewhat unexpected because the *cis* geometry of the chelating amine destroys the planar π -electron system of the NiS₄ unit, which is said to be largely responsible for its stability.¹³

The formation constant of the phen adduct of Ni(dtp)₂ is around 400 times larger than that of the bpy adduct (Table I). In comparison, the formation constant for the addition of phen to Ni(phen)₂²⁺ in water is only around 16 times larger than for bpy. The large stability difference of the phen and bpy adducts of Ni(dtp)₂ may explain why the formation of the bpy adduct of Ni(dtc)₂ could not be observed; by extrapolation, its formation constant in toluene would only be around 6 M⁻¹.

The rather low stability of the amine adducts of Ni(dtc)₂ as compared to those of Ni(xan)₂ and Ni(dtp)₂ is mainly due to a less negative enthalpy of formation of the Ni(dtc)₂ adducts and not to entropy effects (Table I). In turn, one is tempted to interpret this in terms of a comparatively small Ni–N bond energy in Ni(dtc)₂·phen but—as the kinetic experiments below will show—unfavorable solvation effects for the formation of the complex seem to be an important reason for its low stability.

Formation of the *o*-Phenanthroline Adduct of Bis(diethyldithiocarbamato)nickel(II) in Various Solvents. The formation constant of Ni(dtc)₂·phen depends on the solvent (at 298 K): $K(\text{toluene}) = 2237$ M⁻¹, $K(\text{acetone}) = 1126$ M⁻¹, $K(\text{chloroform}) = 96$ M⁻¹ (Table IV). In order to appreciate the various effects of solvation, the Born-Haber cycle given in Scheme I will be considered. Table II lists the enthalpy, entropy, and free energy values of the reactions according to Scheme I. Obviously, ① is solvent-independent and its variation, if computed with the other values of the cycle, is an indication of the consistency of the data.

The formation of Ni(dtc)₂·phen(soln) (⑤) is more exothermic in toluene than in acetone mainly because of the smaller enthalpy of solvation of Ni(dtc)₂·phen (④) in toluene than in acetone. According to Gutmann¹⁴ acetone is a much better donor than toluene; nevertheless, the solvation enthalpies of the electrophile Ni(dtc)₂ (②) are similar in both solvents.

The strong interaction between chloroform and *o*-phenanthroline as indicated by the precipitation of phen·CHCl₃(s) from oversaturated solutions manifests itself again in the negative enthalpy of solution of *o*-phenanthroline in chloroform.

The feature of the entropy values of Table II is that they are all more positive in acetone than in toluene. This may be interpreted by a breakdown of the hydrogen bridge structure of acetone caused by the solute. The more positive entropy of formation of the phenanthroline adduct in acetone compensates

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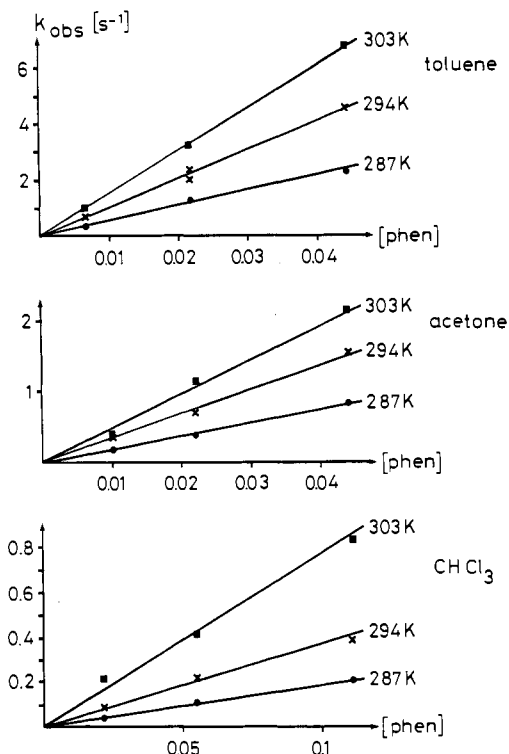


Figure 4. Pseudo-first-order rate constant, k_{obs} , of the reaction $Ni(dtc)_2 + phen \rightarrow Ni(dtc)_2 \cdot phen$. $[Ni] = 2.25 \text{ mM}$.

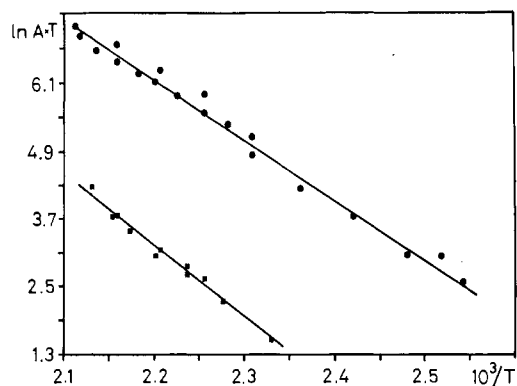


Figure 5. van't Hoff plots according to eq 2: (●) *o*-phenanthroline(l) \rightarrow *o*-phenanthroline(g) ($d = 1 \text{ cm}$); (■) $Ni(dtc)_2 \cdot phen(s) \rightarrow Ni(dtc)_2(s) + phen(g)$ ($d = 10 \text{ cm}$).

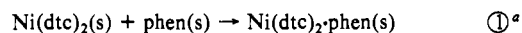
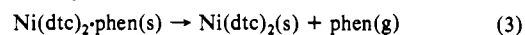
its smaller enthalpy of formation, resulting in rather similar free energies of formation in both solvents, acetone and toluene.

In acetone and toluene ΔG° of the reactions ②, ④, and ⑤ are similar, but the solvation energy of phenanthroline (③) is larger in toluene than in acetone. In the course of the addition of phen to $Ni(dtc)_2$, solvated phen will lose its solvation shell and ΔG° of this desolvation will be more negative in toluene than in acetone, thus contributing more to the stability of $Ni(dtc)_2 \cdot phen$ in toluene than in acetone.

Due to the high solubility of $Ni(dtc)_2$ and $Ni(dtc)_2 \cdot phen$ in chloroform the thermodynamic values of their dissolution are less dependable and we refrain from a detailed interpretation, noting only that the enthalpies and entropies of solution are substantially smaller in chloroform than in acetone and that the higher stability of $Ni(dtc)_2 \cdot phen$ in acetone as compared to that in chloroform is related to a less negative entropy of reaction in acetone.

In each solvent the free energies of solvation of $Ni(dtc)_2$ (②) and $Ni(dtc)_2 \cdot phen$ (④) are similar but slightly less positive for $Ni(dtc)_2 \cdot phen$ than for $Ni(dtc)_2$. This favors the formation of $Ni(dtc)_2 \cdot phen$.

Table III. Thermodynamic Values of the Reactions



	ΔH° , kJ mol ⁻¹	ΔS° , J K ⁻¹ mol ⁻¹	ΔG°_{298} , kJ mol ⁻¹
(4)	106.2 \pm 5	173.5 \pm 10	54.5 \pm 8
(5)	15.1 \pm 2	38.6 \pm 0.5	3.6 \pm 0.4
(6)	54.7 \pm 5	100 \pm 10	24.9 \pm 8
①	-36.4 \pm 7	-34.9 \pm 14	-26.0 \pm 11
① ^b	-34.1 \pm 13	-39.7 \pm 17	-10.8 \pm 2 -22.3 \pm 14 ^b

^a① = (4) + (5) - (3). ^bAverage from Table II. ^cCalculated by using average ΔH° and ΔS° from Table II.

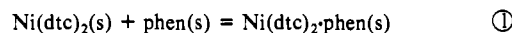
Table IV. Rates of Formation and Stability of $Ni(dtc)_2 \cdot phen$ in Various Solvents at 298 K

	toluene	acetone	chloroform
K , M ⁻¹	2237	1126	96
k_f , M ⁻¹ s ⁻¹	123	43	5.5
$k_d = k_f/K$, s ⁻¹	0.055	0.038	0.057

Table V. Thermodynamic and Kinetic Parameters of the Phenanthroline Association with $Ni(dtc)_2$ in Various Solvents

solvent	ΔH° , kJ mol ⁻¹	ΔS° , J K ⁻¹ mol ⁻¹	ΔG° , kJ mol ⁻¹	$Ni(dtc)_2 + phen$	
				$\sum \Delta H_{solv}$, kJ mol ⁻¹	$\sum \Delta G_{solv}$, kJ mol ⁻¹
toluene	45.0	-53.8	61.0	38.7	18.9
acetone	47.7	-53.5	63.6	40.4	12.7
chloroform	62.9	-19.9	68.7	5.9	<6.7

In Table II the thermodynamic values of the solid-state reaction ① have been calculated from solution data. They may be



compared with values obtained from the reaction sequence of Table III. Within the (rather large) error limits, fair agreement of the two series of values is observed. The main difference in the thermodynamic values of the formation of $Ni(dtc)_2 \cdot phen$ in the solid (table III, ① column) and in solutions (table II, ⑤ column) is the much less negative entropy of the solid-state reaction. This is expected because solids have no translational degree of freedom to be reduced in the course of the reaction while the combination of two reactants in solution diminishes their translational entropy. The enthalpy of complex formation is mostly due to changes in bond energy and thus will be similar in solution and in the solid.

UV/Vis Spectra. The UV/vis spectrum of $Ni(dtc)_2$ corresponds to the one reported by Cavell, Magee, and Hill.¹⁵ These authors report also the spectrum of bis(*N,N*-bis(2,2,2-trifluoroethyl)di-thiocarbamato)nickel(II), (abbreviated $Ni(F_3dtc)_2$), and its adduct with 4-picoline.¹⁶ Upon addition of 4-picoline the band of $Ni(F_3dtc)_2$ at 633 nm ($d_{x^2-y^2} \rightarrow d_{xy}$) suffers a bathochromic shift to 654 nm and a loss of intensity from $\epsilon = 120 \text{ M}^{-1} \text{ cm}^{-1}$ to $\epsilon = 80 \text{ M}^{-1} \text{ cm}^{-1}$. The amines in $Ni(F_3dtc)_2(\text{pic})_2$ are certainly trans to each other while the two nitrogens in $Ni(dtc)_2 \cdot phen$ are cis.

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Table VI. Stability Constants and Rate Constants for the Diamine Addition to Square-Planar Nickel Complexes at 298 K

complex	amine	solvent	log K	log k_f	log k_d	ref
Ni(xan) ₂	bpy	benzene	6.2	4.53	-1.67	3
Ni(dtp) ₂	bpy	benzene	6.43	4.00	-2.43	4
		acetone		4.30		4
Ni(Sacac) ₂	phen	toluene	4.43	2.67	-1.83	5
Ni(dtc) ₂	phen	toluene	3.35	2.09	-1.26	this work

It is therefore not surprising that the spectral changes in the course of the picoline addition to Ni(F₃dtc)₂ and of the phenanthroline addition to Ni(dtc)₂ are different. Indeed, the addition of phen to Ni(dtc)₂ produces a hypsochromic shift from 635 to 600 nm and an increase of ϵ from 80 to 135 M⁻¹ cm⁻¹, only slightly dependent on the solvent. In agreement with ref 16 we find that the intensity of the CT band around 400 nm is reduced by the addition of amine. This feature has been used to check the equilibrium constants in very dilute solutions.

Kinetics. The rate constant k_f for the addition of phenanthroline to Ni(dtc)₂ and the rate constant k_d for the dissociation of Ni(dtc)₂·phen are related to the equilibrium constant K of reaction 1: $K = k_f/k_d$.

The addition of phen to Ni(dtc)₂ is thought to occur in two steps (Figure 1). First, phen is bound with one nitrogen to a coordination site above the NiS₄ plane. Second, one sulfur moves to the position trans to the first nitrogen and the chelate ring of phen is closed.

With the steady-state approximation

$$d[S_4NiN-N]/dt = 0$$

the rate is

$$d[S_4NiN_2]/dt = k_f[S_4Ni][N-N] - k_d[S_4NiN_2]$$

with

$$k_f = k_1k_2/(k_{-1} + k_2)$$

$$k_d = k_{-1}k_{-2}/(k_{-1} + k_2)$$

Two limiting cases may be discussed. (a) The formation of the five-coordinate intermediate is rate determining; then $k_f = k_1$, $k_2 \gg k_{-1}$, and $k_d = k_{-1}/K_2$. (b) The rearrangement of the coordination sphere in the course of the chelate ring closing of phen is rate determining; then $k_{-1} \gg k_2$ and $k_f = k_2K_1$, $k_d = k_{-2}$.

We observe that K and k_f depend strongly on the solvent (Table IV). This fits a mechanism according to (a) because the first step (k_1) certainly involves more rearrangement of the solvation sheath than the second (k_2). The observation that the dissociation of Ni(dtc)₂·phen, k_d , is almost independent of the solvent does not allow us to distinguish between cases a and b. In support of the formation of the five-coordinate intermediate as the rate-limiting step some arguments shall be presented that illustrate the important role of solvation.

The energy of dissolution corresponds to the sum of the lattice energy and the solvation energy. Therefore, the solubility of a compound in different solvents allows us to compare its solvation

energies in these solvents. In order to discuss the influence of solvation on the kinetics of the formation of Ni(dtc)₂·phen we shall compare solvation energies and activation energies.

The more positive the sum of the enthalpy of solvation of Ni(dtc)₂ and of phen, the weaker the interaction between the solvent and these reactants and the less energy needed to "desolvate" them in forming the intermediate S₄NiN-N. The entries in Table V show that the enthalpies of solvation of the reactants and the activation energies for the formation of the adduct are similar in toluene and acetone while a smaller enthalpy of solvation (=stronger solute-solvent interaction) in chloroform corresponds to a larger activation enthalpy.

The free energy of solvation of the reactants decreases in the sequence toluene > acetone > chloroform. This sequence, then, corresponds to an increasing solute-solvent interaction and thus to an increased free energy of activation, i.e. to a slower reaction.

For the reactants to reach the transition state, steric, electronic, and solvation-sheath rearrangements are required. Our results stress the importance of the last of these factors.

The negative activation entropy agrees with an association as the rate-limiting step, and the least negative ΔS^\ddagger in chloroform suggests that in this solvent the disorder following the "desolvating" of the reactants to form the intermediate is particularly large.

Considering other systems similar to that of this study, one will find as a common feature that k_d varies much less than k_f and that k_f is proportional to K (Table VI). If the rate-controlling step of the dissociation of these complexes is the loosening of a Ni-N bond, the small variation of k_d might indicate that the Ni-N bond energies of these complexes are similar. In contrast to our results, Grant and Magee⁴ find that the kinetics of the addition of bpy to Ni(dtp)₂ depends very little on the solvent. To account for the observed second-order kinetics, they assume the first step of the reaction to be the formation of a weak outer-sphere complex of the reactants. The rate-controlling step would be the formation of the five-coordinate intermediate, and the activation energy would reflect the important electronic and steric rearrangements taking place in the course of its formation. If for the formation of Ni(dtc)₂·phen both energy barriers would have to be surmounted to form the five-coordinate intermediate, i.e. the "desolvation" of the reactants as indicated by our results and the steric and electronic rearrangements as indicated by the results of ref 4, this could explain the comparatively slow formation of Ni(dtc)₂·phen and thus its rather low stability.

Conclusion

Kinetic and equilibrium measurements of the formation of Ni(dtc)₂·phen in various solvents, supplemented by solubility and vapor pressure measurements, have allowed us to rationalize the strongly solvent-dependent stability of this complex in terms of relative solvation enthalpies and entropies of the reaction partners.

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