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Spectroscopic and Thermodynamic Studies on Solvatochromic Nickel(II) Complexes

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Summary. The solvatochromic and thermochromic behaviour of a series of mixed Ni(II) complexes with unsubstituted and substituted β-diketones and diamines in the solvents 1,2-dichloroethane (*DCE*), acetonitrile (*An*), acetone (*AC*), *n*-butanol (*n-Bu*OH), formamide (*FA*), N,N-dimethylformamide (*DMF*), dimethylsulfoxide (*DMSO*) and pyridine (*PY*) has been studied and characterized on the basis of electronic spectra. Spectrophotometric methods have been used to evaluate equilibrium constants and their enthalpic and entropic terms for the formation of $\mathrm{Ni}(\beta\text{-}dik)(diam)L^+$ and $\mathrm{Ni}(\beta\text{-}dik)(diam)L_2^+$. Increasing donor strength of the donor-solvents (*L*) and (or) increasing electronwithdrawing parameters of the substituents at the β-diketone and the diamine ligands lead to increasing formation constants, paralleled by relative increase in the stability of the five-coordinated species $\mathrm{Ni}(\beta\text{-}dik)(diam)L^+$. The results are discussed in terms of the extended donor-acceptor concept.

Keywords. Nickel(II) complexes; Solvatochromism; Thermochromism; β-Diketones; Diamines.

Spektroskopische und thermodynamische Untersuchungen an solvatochromen Nickel(II)-Komplexen

Zusammenfassung. Das solvatochrome und thermochrome Verhalten einer Serie gemischter Ni(II)-Komplexe mit unsubstituierten und substituierten β-Diketonen und Diaminen wurde in den Lösungsmitteln 1,2-Dichlorethan (*DCE*), Acetonitril (*An*), Aceton (*AC*), *n*-Butanol (*n-Bu*OH), Formamid (*FA*), N,N-Dimethylformamid (*DMF*), Dimethylsulfoxid (*DMSO*) und Pyridin (*PY*) untersucht und charakterisiert. Spektrophotometrische Methoden wurden verwendet, um Gleichgewichtskonstanten sowie enthalpische und entropische Anteile bei der Bildung von $\mathrm{Ni}(\beta\text{-}dik)(diam)L^+$ und von $\mathrm{Ni}(\beta\text{-}dik)(diam)L_2^+$ zu bestimmen. Zunehmende Donorstärke des Lösungsmittels (*L*) und (oder) zunehmende elektronenziehende Eigenschaften der Substituenten am β-Diketonat- bzw. am Diamin-Liganden führen zu einer Stabilisierung des fünffach koordinierten Komplexes $\mathrm{Ni}(\beta\text{-}dik)(diam)L^+$. Die Ergebnisse werden auf der Basis des erweiterten Donor-Acceptor-Konzeptes diskutiert.

Introduction

Mixed Ni(II) complexes with a β-diketone and a diamine are known to exhibit solvatochromism and thermochromism [1 – 13]. The former can be described as being due to complex formation of donor-solvent molecules (*L*) with the Ni(II)-coordination center according to the equation:

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$$\underset{\substack{\text{square planar}\\ \text{diamagnetic}\\ \text{red}}}{[\mathrm{Ni}(\beta\text{-}dik)(diam)]^{+}} + 2L \rightleftharpoons \underset{\substack{\text{octahedral}\\ \text{paramagnetic}\\ \text{blue or green}}}{[\mathrm{Ni}(\beta\text{-}dik)(diam)L_2]^{+}}.$$

In strong donor solvents such as *DMSO* or *DMF* as well as at low temperature the solution is blue or green, whereas in weak coordinating solvents such as *DCE* or *NE* as well as at high temperature the solution is red. In solvents of medium donor numbers such as alcohol or acetone the two species coexist with intermediate colors [1, 9]. In this paper a more detailed study is provided including solvent and substituent-effects [1, 10, 12] both at the β-diketonate and at the diamine ligands.

Experimental Part

Chemicals were obtained from Merck and Rathburn Chemicals. Mixed Ni(II) complexes with the β-diketones: acetylacetonate (*acac*), benzoylacetonate (*bzac*), dibenzoylmethane (*dbm*), dipivaloylmethanate (*dipm*) and trifluoroacetonate (*tfac*) and the diamines: N,N,N′,N′-tetramethylethylendiamine (*tmen*), N,N,N′-tri-methylethylendiamine (*Me$_3$en*), N,N,N′,N′-tetraethylethylendiamine (*teen*), N,N,N′-triethylethylendiamine (*Et$_3$en*), 1,2-dipiperidinoethane (*dipe*) and N-methyl-1,4-diacacycloheptane (*medach*) have kindly been provided by Prof. Fukuda. The investigated complexes are listed in Table 1.

Solvents have been purified according to standard procedures [14, 15]. Acetone (*Ac*) was heated with $KMnO_4$, refluxed over anhydrous $CaSO_4$, and finally distilled. Pyridine (*PY*) was purified by heating under reflux over potassium hydroxide pellets and then distilled with careful exclusion of moisture. 1,2-Dichloroethane (*DCE*) and Nitroethane (*NE*) were distilled twice, dried over 3Å molecular sieve and finally distilled using a 1 000 mm Vigreoux-column. The water content of the used solvents was found (except the ketones) to be below 30 mg/l by means of Karl-Fischer titration. Acetonitrile (*An*), *n*-butanol (*n-Bu*OH), N,N-dimethylformamide (*DMF*), dimethylsulfoxide (*DMSO*) and formamide (*FA*) were of spectral grade.

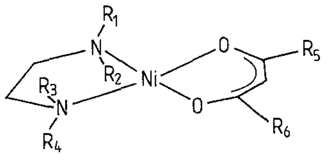
Visible spectra were obtained by means of a Tracor Northren TN-1170 spectralphotometer from Photo-Applied Physics Corporation and a Hitachi U-2000 Spectrophotometer using a cell with a pathlength of 3 cm, thermostated by means of a Haake F4-Thermostat. The temperature within the cell was measured before and after recording the spectra.

To a $3 \cdot 10^{-3}$ molar stock solution of the Ni-complexes in the solvents *DCE* or *NE* the donor-solvent (when necessary diluted with *DCE* or *NE*) was added in a titration procedure. Up to ten recorded spectra were stored in a multichannel memory unit. The obtained spectral titration curves were fitted by means of a combined Marquardt Newton method [16] to evaluate K_1 and K_2 (see below) as well as $\varepsilon_{\mathrm{Ni}L}$.

Results and Discussion

The present investigation is based on the differences in spectral properties of the square-planar and the octahedral species. In the weak donor-solvents *DCE*, and *NE* the complexes show a strong band near 490 nm assigned to a ${}^1A_{2g} \leftarrow {}^1A_{1g}$ (i.e. $d_{x^2-y^2} \leftarrow d_{xy}$) transition of a square planar Ni(II) complex [17–19]. In strong donor solvents two absorption bands appear namely near 1 000 nm and near 615 nm (Fig. 1) indicating an octahedrally surrounded Ni-coordination center. These bands can be assigned to a ${}^3T_{2g} \leftarrow {}^3A_{2g}$ transition (corresponding directly to Δ_0) and to a ${}^3T_{1g}(F) \leftarrow {}^3A_{2g}$ transition, respectively. The shoulder near 450 nm may be associated to the ${}^1T_{2g}(P) \leftarrow {}^3A_{1g}$ transition. In *DCE*-solutions the spectra of the complexes are similar to those in the solid state. The small absorption band observed for the octahedral complexes at 800 nm may be assigned to a ${}^1E_g \leftarrow {}^1A_{2g}$ transition.

Table 1. Position of substituents at the ligands in the investigated mixed Ni(II) complexes



No.	Complex	Mol. weight	R_1	R_2	R_3	R_4	R_5	R_6
1	Ni(*acac*)(*tmen*)$\mathrm{B\Phi_4}$	594.28	*Me*	*Me*	*Me*	*Me*	*Me*	*Me*
2	Ni(*bzac*)(*tmen*)$\mathrm{B\Phi_4}$	655.33	*Me*	*Me*	*Me*	*Me*	*Me*	Φ
3	Ni(*dbm*)(*tmen*)$\mathrm{B\Phi_4}$	717.40	*Me*	*Me*	*Me*	*Me*	Φ	Φ
4	Ni(*tfac*)(*tmen*)$\mathrm{B\Phi_4}$	648.25	*Me*	*Me*	*Me*	*Me*	*Me*	CF_3
5	Ni(*dipm*)(*tmen*)$\mathrm{B\Phi_4}$	678.44	*Me*	*Me*	*Me*	*Me*	*t-Bu*	*t-Bu*
6	Ni(*acac*)(*Me_3en*)$\mathrm{B\Phi_4}$	580.25	*Me*	*Me*	*Me*	H	*Me*	*Me*
7	Ni(*acac*)(*teen*)$\mathrm{B\Phi_4}$	650.39	*Et*	*Et*	*Et*	*Et*	*Me*	*Me*
8	Ni(*acac*)(*Et_3en*)$\mathrm{B\Phi_4}$	622.33	*Et*	*Et*	*Et*	H	*Me*	*Me*
9	Ni(*acac*)(*dipe*)$\mathrm{B\Phi_4}$	674.41	$(CH_2)_5$[a]		$(CH_2)_5$[a]		*Me*	*Me*
10	Ni(*acac*)(*medach*)$\mathrm{B\Phi_4}$	590.25	*Me*	$(CH_2)_2$[a]		H	*Me*	*Me*

[a] Bridging substituent

The d – d band positions and the corresponding molar absorptions are shifted by change of the solvent as well as by change in substituents either at the β-diketonate or at the diamine ligand (see Table 2).

Fig. 2 shows an example of the spectra obtained in the course of the titration procedure of Ni(*acac*)(*dipe*)$\mathrm{B\Phi_4}$. The absorption value found at the maximum of the absorption band of the square planar species decreases on addition of donor-solvents and this has been used to evaluate the respective equilibrium constants. The isosbestic point near 600 nm holds for all substances and for all solvent-ligands investigated. On the other hand the isosbestic point near 450 nm vanishes for some of the substituents, especially when *NE* was used as solvent (Fig. 2). This fact as well as least-square evaluation of the titration curves show that the coordination of donor solvent molecules proceeds via a two-step process involving a five-coordinated species,

$$[\mathrm{Ni}(\beta\text{-}dik)(diam)]^+ + L \overset{K_1}{\rightleftharpoons} [\mathrm{Ni}(\beta\text{-}dik)(diam)]\mathrm{L}^+$$

and

$$[\mathrm{Ni}(\beta\text{-}dik)(diam)]\mathrm{L}^+ + L \overset{K_2}{\rightleftharpoons} [\mathrm{Ni}(\beta\text{-}dik)(diam)]\mathrm{L}_2^+ .$$

The resulting equilibrium constants K_1 and K_2 are listed in Table 3.

The five coordinated intermediate appears to be more stable in *NE* than in *DCE* indicating a weak coordination of *NE* towards the coordinating center. The five coordinated intermediate is further stabilized by increasing donor-strength of

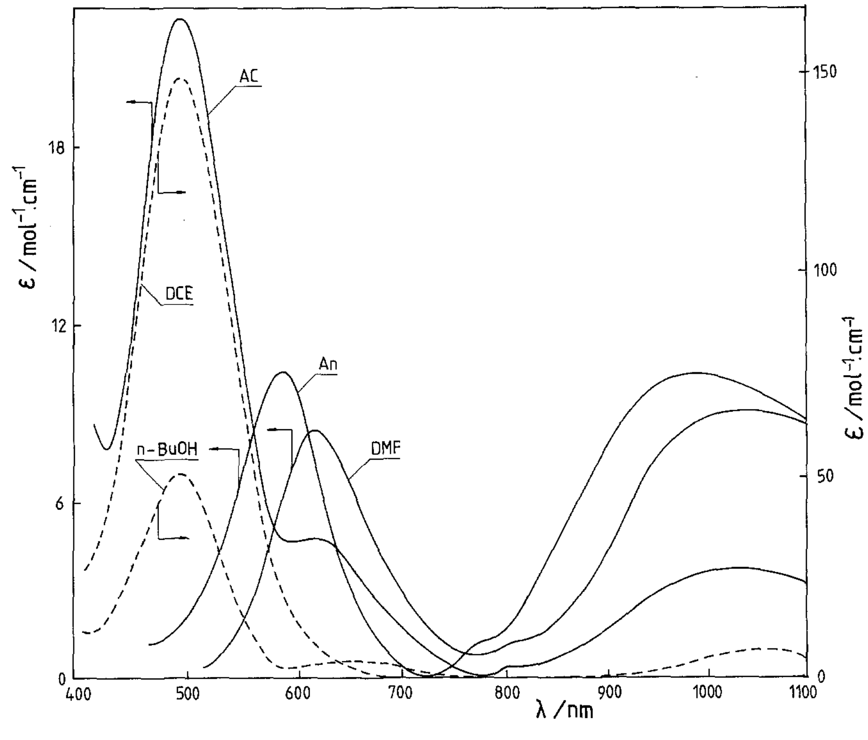


Fig. 1. UV-visible spectrum of Ni(*acac*)(*diam*)$B\Phi_4$ in different solvents at 25°C

L, as seen from the increase in the ratio K_1/K_2. This ratio is also increased by decreasing donor strength of the diamine and the β-diketonate ligands, due to electron withdrawing substituents (see for example *tfac*-complexes).

The UV-visible spectra of Ni(*acac*)(*tmen*)$B\Phi_4$ in *DCE*, *n-Bu*OH, *AC*, *An* and *DMF* (Fig. 1) reveal that the concentration of the octahedral species increases in the order

$$AC < BuOH < An < PY < FA < DMF < DMSO.$$

In the same order K_1, K_2 and β are increased (Table 2). With the exception of *An* and *PY* this series is in agreement with the donor number. The greater *K*-values in *An* may be due to the soft properties of *An* and hence to the development of π-interactions. This interpretation is in agreement with the special differences of copper, and nickel complex in *An*, as Cu^{2+} is softer than Ni^{2+}. In pyridine K_1 and K_2 values are lower than expected. Indeed, pyridine appears to be a weaker donor to various metal ions than would be expected on the basis of donor number [21, 22]. The heats and entropies of transfer of Cu(I) show the same trends for *PY* and for *An* [23].

According to the absorption bands of the octahedral species in the region between 570 to 670 nm the influence of the diketonate substituents is less pronounced than that of the diamine-substituents.

The effect of the substituents of the β-diketonate becomes obvious to the naked eye when the complexes are dissolved in pure *AC* or in *n-Bu*OH. The colour changes from blue for solutions of the Ni(*tfac*)(*tmen*)$^+$ complex to red for the

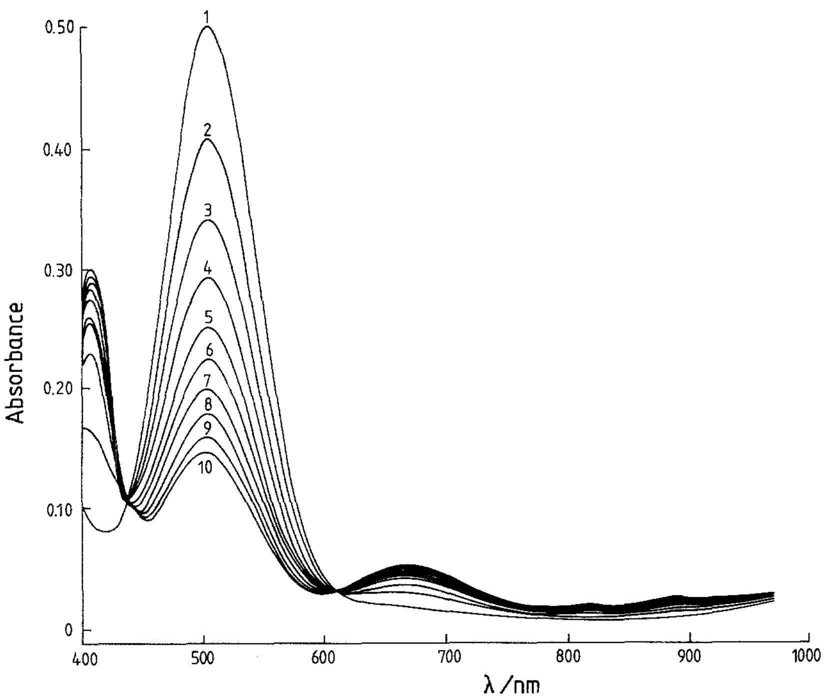


Fig. 2. Spectra of a 2.286 × 10^{-3} molar Ni(*acac*)(*dipe*)$B\Phi_4$ solution in *DCE* with increasing concentrations of *DMF* at 25°C in *DCE*. (*DMF* concentrations in mMol/l: *1* = 0.0, *2* = 1.06, *3* = 2.08, *4* = 3.08, *5* = 4.05, *6* = 5.00, *7* = 5.92, *8* = 6.82, *9* = 7.69, *10* = 8.544

Ni(*dpm*)(*tmen*)$^+$ complex. The values of K_1 and K_2 and hence β increase in the order *dpm* < *acac* < *bzac* ⩽ *dbm* ⩽ *tfac* and this is the order of the increasing electron-attracting and decreasing releasing effects of the groups R_5 and R_6, as shown by plotting the logarithms of the equilibrium constants vs. the Hammett constants σ (Fig. 3). The slope in the Hammett plots is positive, meaning that with increasing electron withdrawing properties of the substituents (paralleled by decreasing Lewis basicity of the amine and diketonate ligands) the formation constants of the five coordinated and the octahedral species is increased [24]. The additivity rule holds also for changes on both ligands [with reference to Ni(*acac*)(*tmen*)$^+$ as the unsubstituted species]. The position of IR-absorption frequency associated with $\nu_{C=O}$ is linearly related to the equilibrium constants. With increasing strength of the C=O bond ($\nu_{C=O}$ = 1 550, 1 578, 1 585, 1 591 and 1 606 cm^{-1} measured at the solid *tmen*-complexes with *dipm*, *acac*, *bzac*, *dbm*, and *tfac*, respectively, i.e. with increasing electron-attracting properties of the β-diketonate) the developing octahedral complex is favoured (Fig. 4). The Ni−O bond strength decreases in the same order. Like in the case of the copper chelates [25] this sequence is related to the order of decreasing electron withdrawing or increasing electron releasing properties of the substituent groups in the β-diketonate ions (with the exception of *dipm*). These findings are in agreement with the predictions of the bond-length variation rules [21].

In Fig. 5 the spectra of Ni(*acac*)(*diam*)$B\Phi_4$ with different substituents at the diamine ligands are given in acetone solution: the square planar complex arrangement is favoured by increasing size of the diamine-group.

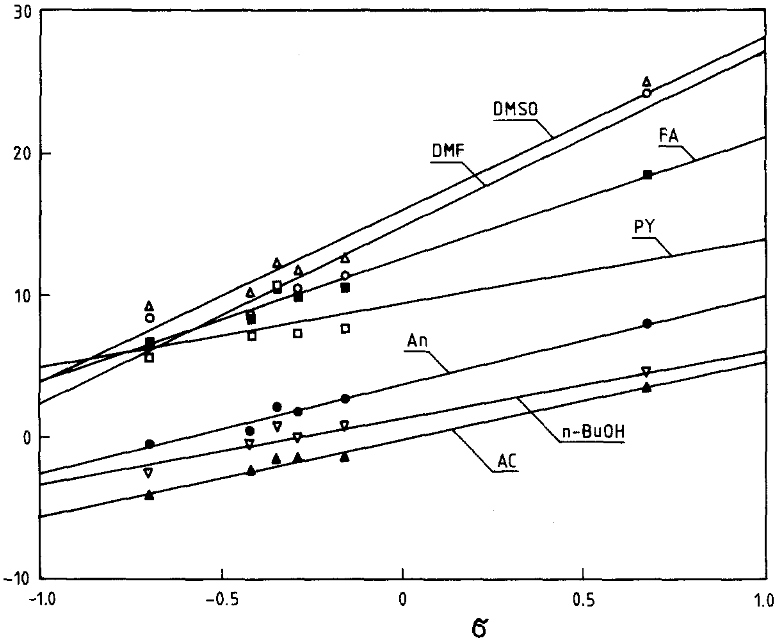


Fig. 3. Hammett plot for overall equilibrium constant $\beta = K_1 * K_2$ for different coordinating donor-solvent at 25°C

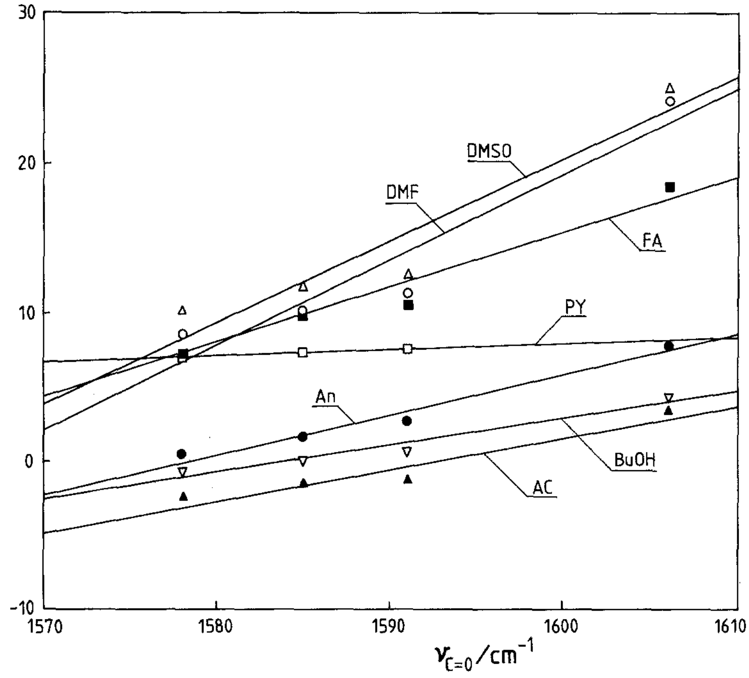


Fig. 4. Overall equilibrium constant β versus $\nu_{C=O}$ IR-absorption frequencies of the complexes

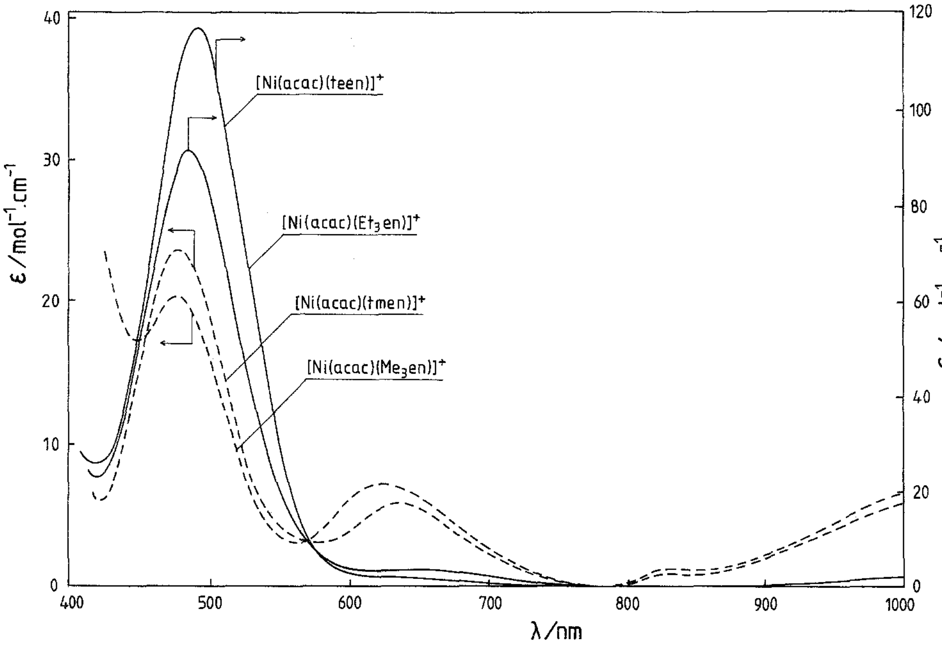


Fig. 5. UV-visible spectrum of different substituted Ni(*acac*)(*diam*)BΦ$_4$ in acetone at 25°C

The substituents at the diamino-ligands are positioned out of plane of the square-planar configuration [1, 9]. Fig. 1 shows that this is not reflected in the absorption bands in the near IR-region. In *DMF* the band near 1 025 nm remains almost unaffected from the substituents. It can be concluded that changes of the β-diketonate substituents influence the ligand field together with the electron-distribution. Change of substituents at the diamines lead to changes in the symmetry of the octahedral complexes. This is also reflected in the low formation constants and in the low ligand field stabilization energies described below.

For a given β-diketonate (for instance *acac*) the equilibrium constants in *An*, *AC* and *n-Bu*OH decrease with the number and the size of alkyl groups in the substituents $R_1 - R_4$ on diamine, namely in the order *Me$_3$en* > *tmen* > *dipe* > *Et$_3$en* > *medach* > *teen*. In the strong donor solvents *FA*, *DMF*, *DMSO*, and *PY* the order is *Me$_3$en* > *dipe* > *tmen* > *Et$_3$en* > *medach* > *teen*. Increasing size of the substituents seems to hinder the solvent coordination. For *teen* and *medach* the octahedral species is formed only in the strong donor solvents. Although this would be expected also for the bulky ligand *dipe* (a ligand weaker than *tmen*) the values of K_1, K_2 and β of [Ni(*acac*)(*dipe*)]$^+$ are higher than those of the respective *teen*, *medach*, *Et$_3$en*, and *tmen* complexes. The steric hindrance to axial coordination appears to be much smaller at the *dipe* complex [26] than in the comparable *teen* complex.

The ligand field strength of the diamines estimated from the values of λ_1 of the octahedral nitrate complexes in *DCE* [26] decrease in the sequence *tmen* > *Et$_3$en* > *dipe* > *teen*. On the other hand, the destabilizing effect decreases in the order *teen* > *medach* > *Et$_3$en* > *tmen* > *dipe*. In general a diamine-ligand with a strong donor property tends to destabilize the octahedrally coordinated com-

Table 2. d-d-Transition and charge transfer absorption bands (in nm) of Ni(β-*dik*)(*diam*)$B\Phi_4$ in $^1A_{2g} \leftarrow {}^1A_{1g}$ (i.e. $d_{x^2-y^2} \leftarrow d_{xy}$) transition of the square planar Ni(II) species; λ_4: Charge transfer band

Complex		*DCE*[a]		*An*		*AC*	
Ni(*acac*)(*tmen*)BF_4	λ_1	–		993	(9.24)	1048	(6.4)
	λ_2	–		594	(9.52)	617	(6.29)
	λ_3	488	(150)	–		475	(23.20)
	λ_4	325	(2712)	301	(1058)	–	
Ni(*bzac*)(*tmen*)$B\Phi_4$	λ_1	–		989	(8.45)	1025	(4.40)
	λ_2	–		595	(9.1)	622	(4.05)
	λ_3	489	(175)	–		490	(23.75)
	λ_4	343	(5353)	331	(1409)	337	(11256)
Ni(*dbm*)(*tmen*)$B\Phi_4$	λ_1	–		984	(8.11)	1042	(7.00)
	λ_2	–		591	(9.76)	618	(7.30)
	λ_3	488	(293)	–		490	(16.83)
	λ_4	374	(11337)	360	(17862)	364	(18600)
Ni(*tfac*)(*tmen*)$B\Phi_4$	λ_1	–		972	(9.82)	1021	(7.23)
	λ_2	–		592	(16.90)	615	(7.38)
	λ_3	493	(142)	–		–	
	λ_4	312	(5883)	308	(8964)	368	(17239)
Ni(*dipm*)(*tmen*)$B\Phi_4$	λ_1	–		979	(11.65)	1025	(7.14)
	λ_2	–		584	(17.11)	624	(sh)
	λ_3	488	(151)	–		490	(67)
	λ_4	330	(2863)	306	(–)	342	(sh)
Ni(*acac*)(*Me*$_3$*en*)$B\Phi_4$	λ_1	–		959	(7.92)	1025	(6.53)
	λ_2	–		580	(8.44)	604	(7.32)
	λ_3	484	(133)	–		473	(20.13)
	λ_4	325	(2658)	302	(9048)	336	(sh)
Ni(*acac*)(*teen*)$B\Phi_4$	λ_1	–		972	(6.78)	–	
	λ_2	–		–		–	
	λ_3	496	(141)	496	(65.60)	496	(112)
	λ_4	317	(2259)	307	(7135)	340	(sh)
Ni (*acac*)(*Et*$_3$*en*)$B\Phi_4$	λ_1	–		984	(6.70)	1058	(3.01)
	λ_2	–		587	(7.43)	625	(4.61)
	λ_3	490	(140)	493	(7.43)	490	(88.12)
	λ_4	327	(2427)	308	(8225)	342	(sh)
Ni (*acac*)(*dpe*)$B\Phi_4$	λ_1	–		1026	(3.31)	1025	(3.23)
	λ_2	–		622	(4.17)	647	(6.93)
	λ_3	496	(89)	–		496	(22.56)
	λ_4	308	(5175)	306	(7299)	383	(sh)
Ni (*acac*)(*medach*)$B\Phi_4$	λ_1	–		967	(6.60)	–	
	λ_2	–		–		–	
	λ_3	472	(137)	474	(62)	473	(114)
	λ_4	322	(3179)	303	(9060)	337	(sh)

[a] Absorption of square planar species

different solvents. λ_1: $^3T_{2g} \leftarrow {}^3A_{2g}$ transition (corresponding directly to Δ_0); λ_2: $^3T_{1g} \leftarrow {}^3A_{2g}$; λ_3: Molar absorption (ε) in $1 \, mol^{-1} \, cm^{-1}$ given in parentheses

*n-Bu*OH	*FA*	*DMF*	*DMSO*	*PY*
956 (2.29)	1026 (8.75)	1025 (8.60)	1055 (8.30)	974 (9.4)
630 (3.32)	623 (8.87)	621 (7.10)	633 (6.13)	584 (11.22)
487 (32)	–	–	–	–
304 (9850)	302 (12100)	302 (11710)	303 (12038)	311 (8955)
956 (3.60)	1025 (4.74)	1025 (7.20)	1048 (8.58)	1007 (12.71)
630 (5.60)	622 (10.66)	618 (7.20)	634 (8.06)	576 (14.75)
490 (19.33)	–	–	–	–
335 (13422)	334 (15000)	337 (9916)	341 (13524)	338 (9242)
1058 (7.43)	1025 (7.78)	1026 (8.84)	1048 (7.67)	983 (8.72)
955 (4.10)	621 (10.37)	623 (8.84)	630 (7.29)	581 (13.33)
628 (6.13)	–	–	–	–
363 (19262)	363 (20058)	366 (11046)	369 (18000)	366 (20883)
1023 (5.91)	989 (12.62)	1025 (13.77)	1024 (10.67)	961 (12.13)
617 (8.96)	592 (24.22)	616 (20.74)	627 (14.77)	589 (20.50)
–	–	–	–	–
311 (12946)	307 (18060)	310 (6419)	305 (12312)	307 (7358)
1048 (6.57)	1025 (8.10)	1025 (8.78)	1051 (8.68)	961 (10.47)
636 (sh)	620 (9.64)	618 (8.12)	632 (7.36)	579 (13.61)
488 (65)	–	–	–	–
304 (34680)	304 (14048)	305 (11443)	307 (12300)	–
1024 (9.23)	1005 (7.10)	1025 (5.97)	1022 (8.70)	986 (8.55)
613 (9.00)	604 (8.98)	607 (5.63)	622 (7.25)	586 (8.77)
–	–	–	–	–
308 (sh)	303 (sh)	304 (5204)	302 (14052)	379 (1012)
1053 (3.42)	1025 (0.37)	>1100 (–)	>1100 (–)	953 (11.57)
–	–	642 (8.24)	670 (6.81)	573 (17.72)
497 (86.40)	496 (54.20)	–	–	–
303 (sh)	–	304 (5666)	305 (8222)	–
1024 (3.57)	1006 (7.24)	1024 (7.42)	1062 (6.50)	972 (7.99)
627 (sh)	620 (9.40)	622 (7.11)	634 (5.71)	583 (8.19)
491 (83)	–	–	–	–
300 (11240)	302 (9931)	305 (7983)	304 (12700)	379 (768)
>1100	1025 (3.47)	>1100	>1100	974 (6.74)
650 (5.62)	643 (9.02)	645 (4.08)	661 (4.05)	589 (7.61)
496 (23.10)	–	–	–	–
301 (2255)	300 (7867)	305 (6305)	301 (10125)	–
1025 (3.28)	1025 (6.46)	1024 (6.46)	1043 (11.03)	974 (6.74)
–	622 (8.92)	624 (6.15)	640 (6.18)	586 (6.42)
472 (87.10)	472 (39.35)	–	–	–
303 (sh)	–	299 (11000)	304 (9723)	385 (1378)

Table 3. Equilibrium constants K_1 and K_2 at 298 K given in mol^{-1}, enthalpies (in kJ/mol) and entropies (in J/mol K) of reaction (2) and reaction (3), respectively, in dichlorethane and in nitroethane

Complex		*An*		*AC*		*Bu*OH	
		K_1	K_2	K_1	K_2	K_1	K_2
Ni(*acac*)(*tmen*)$\mathrm{B\Phi_4}$	K (298 K)	0.138	16.22	0.024	6.50	0.087	11.22
	ΔH	−28.44	−25.77	−44.37	−53.59	−36.46	−33.25
	ΔS	−113.9	−65.13	−181.7	−166.4	−144.6	−93.35
Ni(*bzac*)(*tmen*)$\mathrm{B\Phi_4}$	K (298 K)	0.249	29.45	0.046	5.77	0.110	15.08
	ΔH	−24.54	−28.23	−24.61	−31.35	−35.58	−41.42
	ΔS	−95.00	−67.83	−109.6	−91.95	−139.4	−118.0
Ni(*dbm*)(*tmen*)$\mathrm{B\Phi_4}$	K (298 K)	0.378	30.93	0.0348	8.90	0.107	15.66
	ΔH	−19.13	−24.96	−74.41	−10.38	−37.49	−16.58
	ΔS	−71.60	−54.37	−278.4	−16.76	−144.8	−32.92
Ni(*tfac*)(*tmen*)$\mathrm{B\Phi_4}$	K (298 K)	19.75	265.3	1.86	28.23	3.597	29.39
	ΔH	−49.82	−46.62	−22.39	−31.06	−28.2	−101.9
	ΔS	−144.6	−112.8	−70.94	−79.32	−85.2	−315.9
Ni(*dipm*)(*tmen*)$\mathrm{B\Phi_4}$	K (298 K)	0.074	9.21	0.012	2.23	0.028	3.40
	ΔH	−8.35	−9.19	−42.00	−51.76	−23.7	−39.55
	ΔS	−49.97	−12.72	−179.4	−169.1	−110.0	−124.1
Ni(*acac*)(Me_3en)$\mathrm{B\Phi_4}$	K (298 K)	0.295	32.95	0.051	7.16	0.214	22.92
	ΔH	−26.91	−23.05	−33.24	−40.26	−62.3	−54.2
	ΔS	−101.54	−49.31	−136.08	−120.50	−224.7	−158.0
Ni(*acac*)(*teen*)$\mathrm{B\Phi_4}$	K (298 K)	–	–	–	–	–	–
	ΔH	–	–	–	–	–	–
	ΔS	–	–	–	–	–	–
Ni(*acac*)(Et_3en)$\mathrm{B\Phi_4}$	K (298 K)	0.071	4.68	0.0072	1.294	0.04	2.82
	ΔH	−30.50	−20.01	−72.87	−55.89	−47.7	−35.14
	ΔS	−125.7	−55.07	−288.4	−187.8	−188.5	−110.7
Ni(*acac*)(*dipe*)$\mathrm{B\Phi_4}$	K (298 K)	0.161	6.693	0.0246	0.933	0.029	1.15
	ΔH	−37.63	−33.59	−27.41	−19.51	−18.15	−28.53
	ΔS	−143.40	−98.51	−124.15	−66.97	−91.23	−95.74
Ni(*acac*)(*medach*)$\mathrm{B\Phi_4}$	K (298 K)	–	–	–	–	–	–
	ΔH	–	–	–	–	–	–
	ΔS	–	–	–	–	–	–
Nitroethane							
Ni(*acac*)(*tmen*)$\mathrm{B\Phi_4}$	K (298 K)	0.097	6.07	0.018	0.894	0.075	1.35
	ΔH	−20.20	−9.79	−13.22	−32.95	−27.367	−34.1
	ΔS	−88.33	−18.37	−78.34	−113.34	−114.87	−113.8
Ni(*bzac*)(*tmen*)$\mathrm{B\Phi_4}$	K (298 K)	0.137	17.03	0.034	1.24	0.051	5.954
	ΔH	−38.44	−29.96	−19.56	−22.14	−13.36	−27.71
	ΔS	−147.43	−78.59	−94.66	−73.74	−70.03	−79.83
Ni(*dbm*)(*tmen*)$\mathrm{B\Phi_4}$	K (298 K)	0.319	10.43	0.046	1.754	0.092	6.11
	ΔH	−26.63	−46.39	−13.54	−21.63	−21.03	−29.77
	ΔS	−100.08	−138.37	−71.67	−68.77	−91.38	−86.18

FA		*DMF*		*DMSO*		*PYOH*	
K_1	K_2	K_1	K_2	K_1	K_2	K_1	K_2
16.17	351.7	21.98	415.9	38.67	733.3	13.21	140.0
−35.60	−16.64	−40.32	−14.35	−23.75	−26.58	−42.71	−28.38
−97.89	−7.85	−112.5	−0.910	−49.78	−34.91	−123.7	−55.33
19.01	1278	22.31	1457	60.27	2328	8.021	211.03
−34.64	−28.44	−24.06	−31.70	−16.16	−24.62	−23.84	−70.94
−92.15	−37.27	−55.43	−47.25	−20.86	−19.21	−62.70	−193.84
16.23	1391	23.06	2584	53.52	3741	5.37	277.8
−22.10	−23.25	−30.86	−30.84	−4.33	−45.92	−22.40	−30.06
−49.48	−16.15	−76.39	−37.15	18.80	−83.63	−59.73	−52.43
$1.1 * 10^4$	$8.9 * 10^3$	$1.6 * 10^6$	$1.8 * 10^4$	$4 * 10^6$	$2.4 * 10^4$	$2 * 10^5$	$2 * 10^5$
−154.1	−99.3	−211.1	173.0	−218.4	98.2	−179.5	140.9
−446.4	413.3	−598.6	669.9	−615.4	417.8	−570.02	580.03
7.54	137.4	17.1	355.5	27.03	463.6	4.55	69.1
−21.5	−28.5	−16.4	−22.8	−14.4	−21.5	−23.9	−34.6
−56.1	−55.8	−32.13	−28.4	−21.36	−22.02	−67.9	−82.2
34.2	1317	33.9	1422	80.6	3334	38.1	1562
−31.96	−30.3	−25.9	−20.6	−26.9	−35.5	−31.7	−36.9
−78.6	−42.6	−58.91	−9.3	−55	−53.5	−77.5	−64.5
0.465	3.54	1.49	20.86	2.34	22.11	6.23	233.9
−37.32	−75.40	−14.77	−27.88	−18.85	−19.51	−22.03	−22.7
−134.62	−248.26	−46.81	−69.32	−56.97	−40.56	−59.65	−32.3
8.48	104.0	11.89	181.6	20.53	406.0	11.76	282.3
−23.7	−63.52	−14.35	−42.26	−17.8	−16.17	−36.85	−28.01
−62.7	−176.7	−27.8	−100.1	−34.78	−4.92	−102.34	−48.1
21.74	1961	66.0	2962	321.5	12173	21.9	695.7
−26.1	−28.1	−30.6	−28.5	−18.8	−113	−27.4	−33.9
−65.1	−35.1	−69.6	−30.9	−15.7	−304.9	−67.8	−60.9
1.06	6.05	1.81	20.17	4.63	45.3	13.11	249
−37.31	−47.8	−26.8	−25.13	−12.42	−18.1	−24.81	−25.7
−126.33	−147.7	−85.0	−59.46	−29.52	−29.7	−63.2	−41.8
9.30	240.6	9.19	227.5	18.17	498.7	–	–
−16.53	−30.10	−17.43	−24.50	−20.73	−26.10	–	–
−37.75	−57.1	−41.02	−38.36	−46.60	−37.26	–	–
16.15	334.6	16.83	497.2	39.10	1533	–	–
−24.33	−27.19	−34.68	−36.59	−22.29	−36.01	–	–
−61.88	−44.57	−95.17	−73.40	−45.71	−61.88	–	–
11.25	647.4	15.98	1334	27.14	2763	–	–
−19.36	−35.64	−37.60	−30.14	−40.76	−46.75	–	–
−45.67	−67.49	−104.8	−42.82	−111.1	−92.96	–	–

plexes. However, the sequence of equilibrium constants of the former does not coincide with that of the latter, and this suggests steric influence of the bulky substituent group at the N-donor atoms.

The formation of the octahedral species is exothermic [11, 27]. From Table 3 it can be seen that this is also the case for the formation of the five-coordinated species. The ΔH values associated with K_1 are in general similar to that one of K_2, but the entropic contributions differ strongly. The investigated equilibria exhibit negative entropy changes. The entropic contribution disfavors therefore the coordination of solvent-ligands and is more or less overcompensated by the enthalpic contribution. Positive ΔS values are found only for $\mathrm{Ni}(tfac)(tmen)^+$ with *FA*, *DMF*, *DMSO*, and *PY* and for $\mathrm{Ni}(dbm)(tmen)^+$ with *DMSO*. By coordination of solvent-ligands the Ni$-$O and Ni$-$N bonds towards the β-diketones and the diamines are weakened. This allows an increase in the mobilities of the β-diketonate and the diamine ligands by which the loss in entropy due to coordination of the solvent-donors is overcompensated.

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