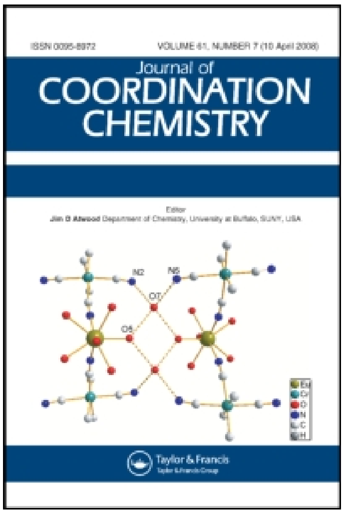

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

FIVE-COORDINATED MIXED LIGAND NICKEL(II) COMPLEXES: THERMODYNAMIC AND SPECTROSCOPIC STUDIES OF SOLVATOCHROMIC AND THERMOCHROMIC PROPERTIES

A. Taha[a]; W. Linert[b]; Y. Fukuda[c]
[a] Department of Chemistry, Faculty of Education, Ain Shams University, Cairo, Egypt [b] Institute of Inorganic Chemistry, Technical University of Vienna, Vienna, Austria [c] Institute of Molecular Science, Coordination Chemistry Laboratories, Okazaki, Japan

To cite this Article Taha, A. , Linert, W. and Fukuda, Y.(1993) 'FIVE-COORDINATED MIXED LIGAND NICKEL(II) COMPLEXES: THERMODYNAMIC AND SPECTROSCOPIC STUDIES OF SOLVATOCHROMIC AND THERMOCHROMIC PROPERTIES', Journal of Coordination Chemistry, 30: 1, 53 — 62

To link to this Article: DOI: 10.1080/00958979308022746

URL: http://dx.doi.org/10.1080/00958979308022746

J. Coord. Chem., 1993, Vol 30, pp. 53–62
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FIVE-COORDINATED MIXED LIGAND NICKEL(II) COMPLEXES: THERMODYNAMIC AND SPECTROSCOPIC STUDIES OF SOLVATOCHROMIC AND THERMOCHROMIC PROPERTIES

A. TAHA†

Department of Chemistry, Faculty of Education, Ain Shams University, Roxy, Cairo, Egypt

W. LINERT*

Institute of Inorganic Chemistry, Technical University of Vienna, Getreidemarkt 9, A-1060 Vienna, Austria

and Y. FUKUDA†

Institute of Molecular Science, Coordination Chemistry Laboratories, Myodaiji-cho, Okazaki 444, Japan

(Received January 13, 1993)

Five-coordinate Ni(II) complexes (Ni(β-dike)(pmdt)X; β-dike$^-$ = acetylacetonate or benzoylacetonate, pmdt = *N, N, N', N'', N''*-pentamethyldiethylenetriamine and X = BPh_4^- or NO_3^-) have been prepared and characterized by vibrational and electron spectroscopy and by magnetic measurements. BPh_4^- complexes are five-coordinate species in non-coordinating solvents like DCE or NM. In solvents with stronger donor properties like DMF or DMSO, or in the case of NO_3^- complexes, octahedral species are formed. Spectrophotometric titration was used to evaluate equilibrium constants between five- and six-coordinated species. Reaction enthalpies and entropies were measured. The latter was found to govern the overall fee energy changes. Steric factors appear to be important when large amine molecules are coordinated to Ni(II).

KEYWORDS: Five-coordinated Ni(II) complexes, solvatochromism, thermochromism, solvent basicity indicators, nonaqueous solvents

INTRODUCTION

Several kinds of square planar, mixed ligand nickel(II) complexes of the form $[Ni(\beta\text{-dike})(diam)]^+$ including an *N, N'*-polyaklylated ethylenediamine (diam) and a β-diketonate (β-dike$^-$) have been synthesized. These complexes are in general

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[†] On leave of absence from home university.

[*] Author for correspondence.

easily soluble in various organic solvents and exhibit solvatochromic and thermochromic properties so that systematic spectroscopic, electrochemical and thermodynamic studies have been performed.[1-8] The chromotropic properties of these compounds are due to reaction (*1*).

$$[\mathrm{Ni}(\beta\text{-dike})(\mathrm{diam})]^+ + 2\mathrm{L} \rightleftharpoons [\mathrm{Ni}(\beta\text{-dike})(\mathrm{diam})\mathrm{L}_2] \qquad (1)$$

L represents a (monodentate) donor ligand such as a donor solvent or a coordinating anion. It has been shown[4-7] that this is essentially a two-step process yielding, depending on the donor strength of L, *cis* or *trans* isomers.[8] Therefore equilibrium constants for (*1*) are not simply related to the Lewis basicity of L expressed for example in terms of the donor number (DN).[8]

In view of an application of such complexes as Lewis base indicators it was of interest to investigate systems where only one donor molecule can coordinate to form a 1:1 complex. This might avoid difficulties arising from the above mentioned two-step process. Using five-coordinated complexes this seemed likely to be done. Accordingly, we synthesized and investigated three mixed ligand nickel(II) complexes of the form Ni(β-dike)(pmdt)X involving the tridentate ligand *N*, *N*, *N'*, *N''*, *N''*-pentamethyldiethylenetriamine (pmdt) and a β-diketonate (benzoylacetonate (bzac$^-$) or acetylacetonate (acac$^-$)).[9-13]

EXPERIMENTAL

Chemicals were obtained from Merck and Rathburn Chemicals. Solvents were purified using standard methods.[14,15] The amines were refluxed over calcium hydride and distilled before use. The water content of the solvents used was found to be below 30 mg dm^{-3} by Karl-Fischer titration (except for the ketones).

Preparation of the complexes

To an ethanolic solution of $\mathrm{Ni(NO_3)_2.6H_2O}$ (10 mmol of nickel salt in 30 cm^3 of EtOH), a mixture of the appropriate β-diketone, (10 mmol of acetylacetone or benzoylacetone) and anhydrous $\mathrm{Na_2CO_3}$ (10 mmol) was added. *N*, *N*, *N'*, *N''*, *N''*-pentamethyldiethylenetriamine (pmdt, 10 mmol in 10 cm^3 of EtOH) was added dropwise with vigorous stirring. After reaction was complete, the green solution was filtered (to separate $\mathrm{NaNO_3}$) and dried in a rotatory evaporator. The crude crystals obtained were recrystallized from 1,2-dichloroethane (DCE) to yield bluish green crystals of the nitrate complex. To prepare tetraphenyloborate complexes, 1 mmol of the respective crude nitrate product was dissolved in hot DCE ($\mathrm{Ni(bzac)(pmdt)NO_3}$ does not crystallize easily and was taken as solution), slightly more than 2 mmol of sodium tetraphenyloborate was added with vigorous stirring and then filtered ($\mathrm{NaNO_3}$). The solution was kept for several days to crystallize in an open beaker. The crude green crystals obtained were recrystallized from DCE (for elemental analyses see Table 1).

Visible spectra were obtained with a Tracor Northern TN-1170 spectrophotometer supplied by Applied Photophysics (Leatherhead, UK) and a Hitachi U-2000 spectrophotometer. Both systems where thermostated by a Haake F4 thermostat. The temperature of the solution was measured before and after recording the spectra. IR spectra were recorded with a Perkin-Elmer IR-spectrophotometer

Table 1 Elemental analyses for the [Ni(β-dike)(pmdt)]X complexes (calculated values in parentheses).

Complex	Color	C[%]	H[%]	N[%]	M.P.[°C]
[Ni(acac)(pmdt)]NO_3	bluish green	48.92(50.28)	8.75(9.04)	16.75(17.32)	160-170
[Ni(acac)(pmdt)]BPh_4	light green	69.48(70.18)	7.53(7.75)	7.21(6.46)	174-176
[Ni(bzac)(pmdt)]BPh_4	light green	73.03(72.49)	7.49(7.36)	6.23(5.90)	178-181

(4000-200 cm^{-1}) using KBr pellets. Far IR spectra (650-50cm^{-1}) were recorded with a Nicolet 20F FT spectrometer using polyethylene pellets. Magnetic moments were obtained by Joy's method by means of a MK1 magnetic susceptibility balance from Johnson Matthey Alfa Products.

To obtain formation constant 4×10^{-3} molar stock solutions of the Ni complexes in DCE were titrated with the donor solvent (when necessary diluted with DCE). Up to ten spectra were recorded and stored in a multichannel memory unit. The obtained titration curves were fitted by means of a combined Marquardt–Newton method[16] to evaluate K and ε_{NiL}. Enthalpy and entropy terms were calculated using from linear regression methods from van't Hoff plots (*i.e.*, lnK *versus* 1/T, $r \geq 0.98$).

RESULTS AND DISCUSSION

Characteristic IR and Far-IR absorption frequencies are given in Table 2. The observed bands are assigned using normal coordinate analysis of similar complexes, namely Ni(acac)2 and of $Ni(acac)_2Py_2$.[17] The spectra of $NaNO_3$ and $NaBPh_4$ were used to identify absorptions due to the anion.[18]

The characteristic IR absorption frequency of the nitrate ion is found to be split into two bands at 1762 cm^{-1} and at 1742 cm^{-1} (v_1 and v_4). The relatively small splitting shows that the nitrate ion acts as a monondentate ligand.[19–23] C=O vibrations are found to be hardly affected by the anion, whereas C=C vibrations are strengthened when BPH_4^- is replaced by NO_3^-. Absorptions associated with Ni-O and Ni-N stretching vibrations are also shifted by the anion (see Table 2).

The electronic spectra of (Ni(β-dike)(pmdt)X dissolved in various organic solvents are summarized in Table 3. The BPH_4^- complex shows in DCE a green color associated with strong absorption bands at 620 nm and at 380 nm. They can be assigned to a $^3B_1(F) \rightarrow {}^3E(P)$ and a $^3B_1(F) \rightarrow {}^3A_2(P)$ transitions, respectively. Two weak bands (or shoulders) near 950 nm ($^3B_1(F) \rightarrow {}^3A_2$)(F) and 764 nm ($^3B_1(F) \rightarrow {}^3B_2(F)$) are also found. These spectra indicate a square pyramidal structure.[13,24] Solutions in strong donor solvents like DMF and DMSO show a blue colour with two absorption bands near 1025 nm and 620 nm indicating octahedral coordination of,[5] *i.e.*, [Ni(β-dike)(pmdt)(L)]$^+$ is present. These bands can be assigned to $^3A_{2g} \rightarrow {}^3T_{2g}$ and $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ transitions, respectively, and are comparable to those of [Ni(β-dike)(diam)$(L)_2$]$^+$ species.[5] The small absorption band observed for the octahedral complexes at about 800 nm may be assigned to a $^3A_{2g} \rightarrow {}^1E_g$ transition.

The molar absorptions of the bands at 620 nm and 387 nm of the NO_3^- species are much lower than those of the corresponding BPh_4^- complexes. This confirms the coordination of the NO_3^- ion. The intensity of the band near 620 nm remains

Table 2 IR absorption frequencies for the [Ni(β-dike)(pmdt)]X complexes and their assignments.

IR-absorption maxima			
[Ni(acac)(pmdt)]BPh_4	[Ni(bzac)(pmdt)]BPh_4	[Ni(acac)(pmdt)]NO_3	Assignment
		1762	υNO_3^-
		1742	υNO_3^-
1580	1587	1582	$\upsilon C=O$
1517	1538		$\upsilon C=C$
1468	1468	1475	$\upsilon C=C$
		1292	υNO_3^-
Far-IR absorption maxima			
624m	624m	627vs	π(diketonate ring)
611vs	611vs	611m	Ring deformatioin, Ni-O[a]
576s	579sh	576s	Ni-O[a]
	533m		π(diketonate ring)
488m	483m	490m	Ni-O[a]
467s	467s		Ring deformation, Ni-O[a]
	451m	451vw	Ni-O[a] + v($C-CH_3$)
436s	426s	422vw	Ni-O[a]
413m	409w	413vw	Ring deformation
398vw	399vw	399m	Ni-O[b]
391m	387m	387vw	Ni-O[a]
342vw	339m	342vw	Ni-O[a]
274s	278m	281m	Ni-O[a]
259m	255s	254w	Ni-O[c]
227m	228m	229m	Ni-N
176w	178m	174m	Ni-N
153m	152m	153s	Ni-N
114m	114w	111m	
104m	104m	100s	
95m	95m	94m	
86w	83w	86s	
75s	65m	75vs	
58m	58s	61s	

vs = very strong, s = strong, m = medium, w = weak, vw = very weak and sh = shoulder.
[a] Stretching vibration.
[b] Asymmetric deformation of β-diketonate plane.
[c] Symmetric deformation of β-diketonate plane.

almost unchanged with increase of donor strength of the solvent from DCE to Ac while it is changed for DMF and stronger donor solvents. This suggests that the former solvents are not able to replace the NO_3^- ion while the latter are strong enough to do this. This agrees with a proposed donor number for the NO_3^- ion (acting as a monodentate) of about 20.[25]

The magnetic susceptibilities of the complexes are (after correction for diamagnetic contributions) 3.23 μ_B, 3.11μ_B, and 3.15μ_B for [Ni(acac)(pmdt)]BPh_4, Ni(bzac)(pmdt)BPh_4 and [Ni(bzac)(pmdt]NO_3, respectively. These values are similar to those found for other five- and six-coordinate Ni(II)-complexes and refer to two unpaired electrons.[3–5] The fact that these complexes are paramagnetic means that with coordination of a donor molecule no change in magnetic properties occur so that no spin barrier has to be overcome. This is different to the case with the square planar [Ni(β-dike)(diam)]$^+$ complexes.

Table 3 Absorption maxima (λ_{max} in nm) and extinction coefficients (ε in $M^{-1}cm^{-1}$) given in parentheses for the spectra of Ni(acac)(pmdt)X complexes in various organic solutions at 25°C.

Complex	DCE	An	Ac	Fa	DMF	DMSO	Py	n–BuNH$_2$
[Ni(acac)(pmdt)]NO$_3$	1058 (15.8)	990 (14.5)	1044 (13.5)		1043 (11.4)	1059 (10.3)	1053 (12.8)	925 (6.0)
	800sh	800sh	800sh		800sh	800sh	806sh	804sh
	626 (27.5)	605 (30)	626(29)		622 (22.8)	628 (21.5)	623 (23.2)	595 (15.9)
	387 (81)	377 (85.6)	386 (87.2)		384 (67.9)	385(69.5)	384(72)	366 (55)
[Ni(acac)(pmdt)]Bo$_4$	945 (12.2)	951 (9.7)	955 (8.22)	1014 (24)	1033(7.7)	1052(13.9)	965(8.6)	1035 (11.5)
	867 (12.6)	872 (7.7)	870 (8.6)					
	785sh	780sh	783sh	787sh	787sh	786sh	783sh	778sh
	620 (47.8)	619 (33)	620 (40.9)	617 (16.8)	616 (11.3)	624 (13.9)	612 (19.8)	582 (10)
	379(322)	377(224)	378(280)	378(105)	358(98)	361sh	376(128.3)	360sh
[Ni(bzac)(pmdt)]Bo$_4$	945 (7.6)	965 (9.1)	910 (10.6)	1020 (20.8)	1022 (20.2)	1052 (12.9)	958 (7.8)	930 (7.4)
	866(9.7)	871 (7.1)	873 (8.1)					
	770 (12.7)	785sh	780sh	789sh	796sh	790sh	778sh	775sh
	620 (43.1)	619 (29.3)	620 (37.9)	616 (13.8)	609 (11.7)	626 (10.6)	607 (17.0)	589 (8.1)

Table 4 Equilibirum constants for reaction (*2*) in DCE at different temperatures; $PrNH_2$ = *n*-proplyamine, $BuNH_2$ = *n*-butylamine, $PeNH_2$ = *n*-pentylamine, H x NH_2 = *n*-hexylamine, *sec*-$BuNH_2$ = *sec*-butylamine, *tert*-$BuNH_2$ = *tert*-butylamine, Pr_2NH = di(*n*-propyl)amine.

	$[Ni(acac)(pmdt)]BPh_4$				$[Ni(bzac)(pmdt)]BPh_4$			
Ligand (L)	283K	293K	303K	313K	283K	293K	303K	313K
An	0.369	0.355	0.346	0.335	0.182	0.155	0.12	0.098
Fa	11.95	11.53	11.02	11.54	13.25	12.79	12.30	11.80
DMF	10.50	9.32	7.99	6.88		11.99	11.55	11.09
DMSO	6.26	5.52	4.42	3.69	6.37	5.53	4.96	4.32
Py	3.73	2.98	1.43		3.93	2.97	2.03	1.19
$PrNH_2$	12.60	10.43	8.80	7.93	12.77	10.63	8.98	7.60
$BuNH_2$	12.0	10.65	8.53	7.24	12.94	11.52	10.13	8.53
$PeNH_2$	13.0	10.26	8.34	7.00	13.52	12.0	10.25	8.63
$HxNH_2$	12.25	11.13	10.25	9.45	16.39	14.96	13.64	12.62
sec-$BuNH_2$	6.45	5.50	3.73	2.64	5.41	4.48	3.76	2.98
tert-$BuNH_2$		1.62	1.43	1.22	1.726	1.517	1.33	1.16
pr_2NH	0.57	0.425	0.34	0.27	2.11	1.74	1.48	1.16

Equilibrium constants according to reaction (*2*)

$$[Ni(\beta\text{-dike})(pmdt)]^+ + L \overset{K}{\rightleftarrows} [Ni(\beta\text{-dike})(pmdt)(L)]^+ \qquad (2)$$

are given in Table 4. In general, these constants are somewhat higher for the benzoylacetonate species than for acetylacetonate complexes. This is in agreement with the basicity of the respective β-diketone (pK_a of bzac$^-$ = 13.25 and of acac$^-$ = 12.75)[26] which leads to stronger election withdrawal and an increase of Lewis acidity of Ni(II). Thermodynamic data (Table 5) show that the formation of the octahedral species is exothermic. Values of both ΔH and ΔS are much smaller than for $[Ni(\beta\text{-dike})(diam)]^+$ complexes. In general, negative entropy changes are found, except for Fa and DMF. The same exceptions are found for coordination to $[Ni(\beta\text{-dike})(diam)]^+$ complexes.[5]

Table 5 Thermodynamic parameters for coordination of a solvent molecule to $[Ni(\beta\text{-dikePh}_4$ (ΔH in kcal mol^{-1}, ΔS in cal mol^{-1} K^{-1}); abbreviations as in Table 4; 1 cal = 4.184J.

	$[Ni(acac)(pmdt)]BPh_4$			$[Ni(bzac)(pmdt)]BPh_4$			
Ligand	K_{298K}	ΔH	ΔS	K_{298K}	ΔH	ΔS	DN
An	0.351	-0.56	-3.95	0.14	-3.71	-16.45	14.1
Fa	11.26	-0.69	-2.49	12.54	-0.68	+2.74	24.0
DMF	8.16	-2.50	-4.13	11.58	-0.71	+2.51	26.6
DMSO	4.97	-3.17	-7.51	5.30	-2.24	-4.24	29.8
Py	2.56	-8.12	-25.9	2.53	-6.94	-21.7	33.1
$PrNH_2$	9.95	-2.75	-4.71	10.0	-3.04	-5.67	45.1[a]
$BuNH_2$	9.61	-3.05	-5.80	10.8	-2.42	-3.43	45.9[a]
$PeNH_2$	9.65	-3.64	-7.78	11.1	-2.64	-4.12	45.9[a]
HNH_2	10.77	-1.52	-0.38	14.4	-1.54	-0.10	46.2[a]
sec-$BuNH_2$	4.56	-5.37	-15.1	4.16	-3.45	-8.80	45.9[a]
tert-$BuNH_2$	1.45	-2.58	-7.83	1.43	-2.33	-7.13	47.9[a]
Pr_2NH	0.40	-4.34	-16.5	1.62	-3.44	-10.6	37.8[a]

[a] Ref. 31.

In Figure 1 logarithms of the formations constants are plotted *versus* donor numbers. It can be seen that the formation constants increase strongly from An to Fa and decrease despite increasing donor properties in the order Fa, DMF, DMSO and Py. They again increase with increasing donor properties for amines, where however, sterical effects appear to be important (see above).

Contrary to this, the ΔH values show the expected behaviour,[5,27,28] namely linear increasing exothermicity with increasing donor strength of the ligand (see Fig. 2) Fa and the amines are strongly structured solvents and yield less negative enthalpy values as part of the reaction enthalpy is due to disruption of the solvent structure. The entropic contribution is responsible for the inverse sequence of the equilibrium constants (*i.e.*, ΔG). ΔS values become more negative with increasing DN and is especially pronounced for solvents like Fa, DMF, DMSO up to Py (Py should be considered as an exception because investigations of $[Ni(acac)(tmen)]^+$ have shown that ligand exchange reactions might take place[5]). In other words, the entropic contributions overcompensate the enthalpic contributions and lead to the observed reversed relationship with the *enthalpy* controlled donor numbers.

The present system may be compared with the square planar $Ni(tmen)(acac)^+$ system. There, consecutive coordination of donor molecules takes place, yielding first a five-coordinate species $[Ni(tmen)(acac)L]^+$ and, in a second step, six-

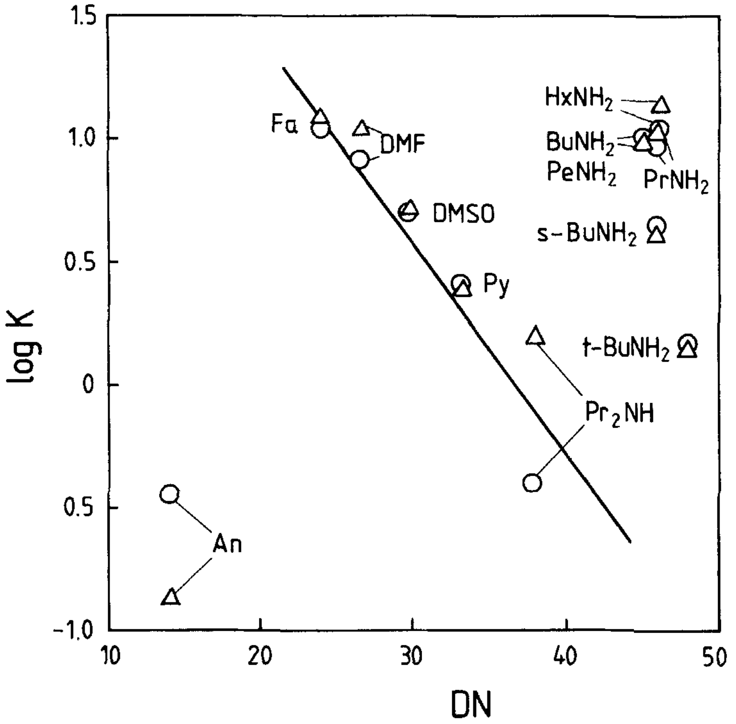


Figure 1 Logarithms of formation constant of six-coordinate species formed by addition of a solvent donor molecule L to $[Ni(acac)(pmdt)]BPh_4$ (Δ) and $[Ni(bzac)(pmdt)]BPh_4$ (O) *versus* donor numbers (DN) (reaction (*2*)).

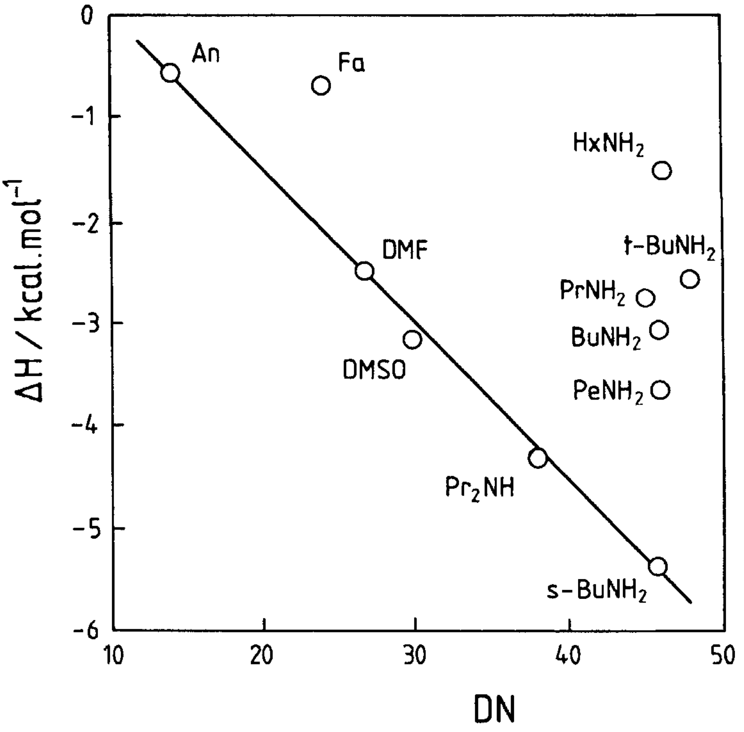
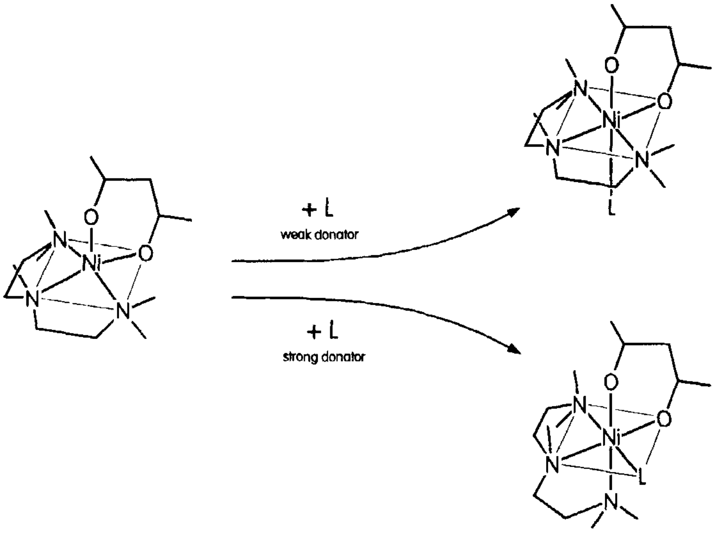


Figure 2 Reaction enthalpies for the reaction $[Ni(acac)(pmdt)]BPh_4 + L \leftrightharpoons [Ni(acac)(pmdt)]\ LBPh_4$ *versus* DN.

coordinate $[Ni(tmen)(acac)(L)_2]^+$. In the case of weak donor molecules, the *trans*-species is formed.[8] According to the bond angle variation rule,[8] increasing donor strength lead to increasing deformation of the tmen–acac plane. In the case of strong donors this seems to force a second donor molecule L to coordinate in a *cis*-position.

In the same way, donor molecules lead to a deformation of the $[Ni(\beta\text{-dike})(pmdt)]^+$ system. It seems likely that the almost planar configuration of the coordinated triamine is retained when weak donor molecules coordinate (An and weaker). However, the system might be reorganized to an out-of-plane configuration when strong donor molecules (Fa and stronger) are coordinated (see Scheme 1). This change in structure and the increasing strain within the triamine and the diketonate rings might explain the abovementioned entropy changes.[8,29,30]

Coordination of the amines is influenced by steric factors especially when bulky dialkyl or *sec*- and *tert*-species are involved. The ratio of the equilibrium constants of *n*-$BuNH_2$ to those of *sec*-$BuNH_2$ is about 2 and the ratio of the constants for *sec*-$BuNH_2$ to *tert*-$BuNH_2$ is about 4. This reflects the sensitivity of this system to steric factors as a result of bulky triamine ligand (pmdt).[31] Reaction enthalpies are lower than expected from the relation with the solvents donor numbers and can be explained by the necessary energy for breaking the internal solvent structure present in amine solvents.



Scheme 1

In conclusion it might be said that although it was hoped that the investigated five coordinate Ni(II)-system would show a more simple pattern of solvatochromic and thermodynamic properties than square planar species, a more complicated pattern is found. The reason for this behaviour, which is expressed in a nonlinear, in part reversed, dependence upon donor properties of the coordinating solvent molecule, is concerned with pronounced entropic changes. These seem to be based on intramolecular bond angle and bond length variations[8] leading to pronounced structural changes. From the point of view of Lewis basicity indicators, the square planar complexes appear to be more straightforward despite the fact that 1:2 coordination can occur. In any case, it seems worthwhile to investigate the analogous five-coordinate Cu system, and especially its solvatochromism which is due on a pronounced Jahn-Teller effect.

Acknowledgements

Thanks are due to the Fonds zur Förderung der wissenschaftlichen Forschung in Österreich for financial support (Project 8795), and to the Ministry of Education of Egypt for the support *via* their "channel-program" for allowing A.T. to carry out this work in Vienne. Financial support by the Austrian Ministry of Science and Research and the Japan Society of the Promotion of Science is gratefully acknowledged. Professor Viktor Gutmann is thanked for many helpful discussions.

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