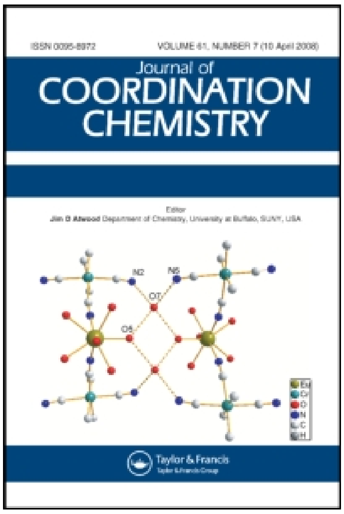

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DINUCLEAR FIVE-COORDINATED MIXED LIGAND COMPLEXES. PART I: INTERACTION OF NICKEL(II) COMPLEXES WITH NONAQUEOUS SOLVENTS

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DINUCLEAR FIVE-COORDINATED MIXED LIGAND COMPLEXES
PART I: INTERACTION OF NICKEL(II) COMPLEXES WITH NONAQUEOUS SOLVENTS

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The dinuclear 5-coordinate Ni(II) complex $[Ni_2(taet)(pmdt)_2]^{2+}$, where taet = 1,1,2,2-tetraacetylethanate and pmdt = *N,N,N′,N′′,N′′*-pentamethyldiethylenetriamine, has been prepared and characterized by vibrational and electron spectroscopy and by magnetic measurements. In non-coordinating solvents such as DCE or NM and with non- or weakly coordinating anions like ClO_4^- or $B\phi_4^-$ these complexes occur as bis-five-coordinate species. In solvents with stronger donor properties (Fa or DMF) and with more strongly coordinating anions, mono- or bis-octahedral species are formed. Spectrophotometric titration was used to evaluate equilibrium constants and associated reaction enthalpies and entropies for the stepwise coordination of donor solvents in DCE. Free energy changes are found to be entropy controlled.

KEYWORDS: nickel(II), chelates, chromotropism, thermodynamic properties, pentacoordination, dinuclear complexes

INTRODUCTION

Mononuclear, 5-coordinate mixed ligand, nickel(II) chelates with a terdentate triamine ligand (namely *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (pmdt)), together with β-diketonates show chromotropic properties[1] and systematic spectroscopic and thermodynamic studies have been reported previously.[2] The stability of the complexes stimulated us to synthesise dinuclear 5-coordinate, nickel(II), mixed

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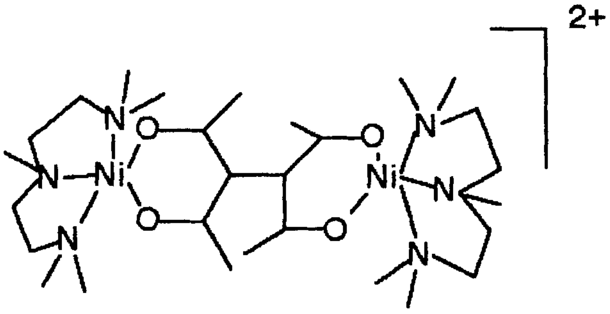
ligand complexes using a tetradentate, namely tetraacetylethanate (taet) together with the mentioned pmdt to form the complexes $Ni_2(taet)(pmdt)_2X_2$ (see I; $X^- = ClO_4^-$, Cl^-, NCS^-, NO_3^- and $B\phi_4^-$). Spectroscopic studies and thermodynamic parameters of these complexes, **I**, were investigated in nonaqueous solutions and compared with results for mononuclear species.[2]



I

EXPERIMENTAL

Chemicals were obtained from Merck and Rathburn Chemicals and used without further purification. Solvents were purified using standard methods.[3] The amines were refluxed over calcium hydride and distilled before use. The water content of the solvents was below 30mg/l (Karl-Fischer titration was used with the exception of the ketones). The respective tetrabutylammonium salts were prepared according to ref. 4. Tetraacetylethane (H_2taet) was synthesized according to published methods.[5]

$[Ni_2(taet)(pmdt)_2](B\phi_4)_2$

A mixture of tetraketone (5mmol) and anhydrous Na_2CO_3 (10mmol) suspended in 20 cm^3 of EtOH was added dropwise with continuous stirring to an ethanolic solution of $Ni(NO_3)_2.6H_2O$ (10mmol of nickel salt in 30 cm^3). The triamine (pmdt) (10mmol in 10 cm^3 of EtOH) was then slowly added with vigorous stirring. When the reaction was complete, the green solution was filtered (to remove precipitated $NaNO_3$) and dried using a rotatory evaporator. The crude crystalline material so obtained was dissolved in hot DCE and slightly more than double the stoichiometric amount of sodium tetraphenylborate added. The solution was vigorously stirred, filtered and kept for two days. Green crystals were obtained and recrystallized from DCE. Elemental analysis yielded C = 69.89 (70.18), H = 7.53 (7.75) and N = 6.62 (6.47)% (calculated values in parentheses).

Visible spectra were obtained by means of a Tracor Northern TN-1170 spectrophotometer and a Hitachi U-2000 spectrophotometer using a cell with a pathlength of 3 cm, thermostatted by a Haake F4 Thermostat. The temperature within the cell was measured before and after recording the spectra. Far IR measurements were recorded with a Nicolet 20 far F IR vacuum spectrometer (FTIR) with a TGS (room temperature) detector using polyethylene wafers. The data collection was accomplished with the Happ-Genzel apodization function. Magnetic moments were obtained using a magnetic susceptibility balance (model MK1 from Johnson Matthey Alfa products).

To obtain formation constants, 4×10^{-3} molar stock solutions of the Ni complexes in DCE were titrated with donor solvent (when necessary diluted with DCE). Up to ten recorded spectra were stored in a multichannel memory unit. The titration curves were fitted by means of a combined Marquardt-Newton method[6] in order to evaluate K and ε.

RESULTS AND DISCUSSION

Characteristic IR and far-IR absorption frequencies of the complexes are given in Table 1. The observed bands are assigned following normal coordinate analyses of similar complexes, namely of $Ni(acac)_2$, $Ni(acac)_2Py_2$[7] and of $Ni(acac)(pmdt)B\phi_4$[2] and using the spectrum of $NaB\phi_4$ to identify absorptions due to the $B\phi_4^-$ anion. The absorption bands are similar for the dinuclear and the mononuclear Ni complexes and hence the mutual interactions between the two Ni coordination centres seem to be small. This is further supported by the magnetic susceptibility of the solid compound which is similar to values found for mononuclear compounds (μ_{eff}/Ni = 3.12 B.M. for $[Ni_2(taet)(pmdt)_2]^{2+}$).

Electronic spectroscopic data for the dimer complex dissolved in various organic solvents are summarized in Table 2. When the chelates are dissolved in DCE they are green and the strong absorption bands at 620 nm and 379 nm can be assigned

Table 1 IR and far-IR absorption frequencies and their assignments for dinuclear and mononuclear five- coordinate nickel(II) complexes.

	IR-absorption maxima	
$[Ni_2(taet)(pmdt)_2](B\phi_4)_2$	$[Ni(acac)(pmdt)]B\phi_4$[a]	Assignment
1577	1580	$^{\nu}$C = O
	1517	$^{\nu}$C = C
1471	1468	$^{\nu}$C = C

	Far-IR absorption maxima	
$[Ni_2(taet)(pmdt)_2](B\phi_4)_2$	$[Ni(acac)(pmdt)]B\phi_4$[a]	Assignment
624m	624m	diketonate ring-deformation
610vs	611vs	Ring deformation, Ni–O[a]
577m	576s	$^{\nu}$Ni–O
487m	488m	$^{\nu}$Ni–O
473s	467s	Ring deformation, $^{\nu}$Ni–O
442s	436s	$^{\nu}$Ni–O
	413m	Ring deformation
	399m	$^{\delta}$Ni–O, ass
388s	391m	$^{\nu}$Ni–O
277m	274s	$^{\nu}$Ni–O
254w	259m	$^{\delta}$Ni–O, sym
228m	227m	$^{\delta}$Ni–N, ass
180m	176w	$^{\nu}$Ni–N
150m	153m	$^{\nu}$Ni–N
98m	95m	

[a] Data taken from reference 2 for comparison; vs = very strong, s = strong, m = medium, w = weak, vw = very weak and sh = shoulder.

Table 2 Absorption maxima (λ_{max} in nm) for the spectra of $[Ni_2(taet)(pmdt)_2](B\phi_4)_2$ with various donor molecules and different anions in DCE solution at 25°C. Molar absorptions ε (in l $mol^{-1}cm^{-1}$) are given in parentheses.

	DCE	An	MeOH	Fa	DMF	DMSO	Py	n-$BuNH_2$	sec-$BuNH_2$
λ_1	1013 (18)	1002 (14)	1022 (12.3)	1058 (14)	1048(14)	1060 (14.6)	985 (14)	980 (12)	980 (5.3)
λ_2	866 (14.6)	866 (16)							
λ_3	785sh	790sh	795sh	780sh	790sh	785sh	780sh	780sh	780sh
λ_4	622 (69)	613 (31)	623 (33)	619 (28)	624 (19)	630 (18)	610 (22)	593 (16.6)	624 (12.0)
λ_5	380 (636)	308sh	380 (296)		380 (57)	380 (168)		380 (198)	

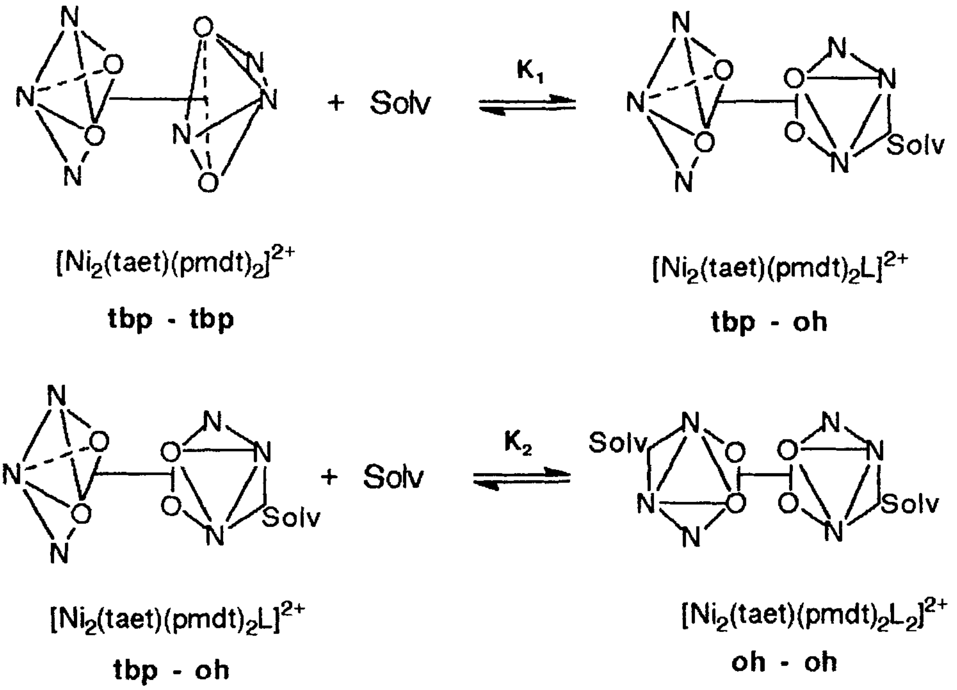
	Cl^-	Br^-	I^-	SCN^-	N_3^-	NO_3^-
λ_1	>1100	>110	1000 (9.7)	>1100	1000 (21.3)	1063 (17)
λ_2	876 (13.3)	–	865 (8.3)			
λ_3	758 (19.3)	826sh	780sh	790sh	803sh	826sh
λ_4	665sh, 540sh	646 (29.0)	633 (30.3)	621 (21.3)	685 (23.0)	610 (36)
λ_5	440 (146.7)					

to $^3B_1(F)\rightarrow{}^3E(P)$ and $^3B_1(F)\rightarrow{}^3A_2(P)$, respectively, with another weak band at 1012 nm, assigned to $^3B_1(F)\rightarrow{}^3A_2(F)$, thus indicating a square pyramidal arrangement around the nickel ion.[1,2,8] Solutions in strong donor solvents like DMF and DMSO are blue and the two absorption bands near 1050 nm and 625 nm indicate an octahedral Ni coordination centre.[9] These bands can be assigned to a $^3T_{2g}\leftarrow{}^3A_{2g}$ and a $^3T_{1g}(F)\leftarrow{}^3A_{2g}$ transition, respectively, and are comparable to those of $[Ni(\beta\text{-dik})(dam)(L)_2]^+$ species.

The spectra of the complex dissolved in DCE in the presence of various tetrabutylammonium halides, pseudohalides or other salts (Table 2) indicate more or less pronounced interaction between the anion and the Ni centre in solution, *i.e.*, the extinction coefficient increases in the sequence $SCN^- \leq N_3^- < Br^- \leq I^- < NO_3^-$. The observed trend follows the donor numbers of anions.[10] The spectra of solutions containing chloride are markedly different and are attributed to the ability of the chloride ion to form bridged and polymeric complexes.

The spectroscopic changes indicate that in solvents of high donor number the solvent molecules combine with the 5-coordinate Ni(II) centre making it 6-coordinate. Equilibrium constants were calculated by least-squares evaluation of the titration curves which show a two-step process involving a mixed five-six coordinate species, as shown below.

The resulting equilibrium constants K_1 and K_2 are listed in Tables 3 and 4. In general, the overall formation constants ($\beta = K_1{*}K_2$) increase with increasing donor



Scheme 2

Table 3 Association constants of $[Ni_2(taet)(pmdt)_2](B\phi_4)_2$ and $[Ni(acac)(pmdt)]B\phi_4$ with different donor molecules and aliphatic amines in DCE solution at different temperatures (K).

		$[Ni_2(taet)(pmdt)_2](B\phi_4)_2$				$[Ni(acac)(pmdt)B\phi_4$[a]			
Ligand		283	293	303	313	283	293	303	313
Fa	K_1	6.64	5.46	4.30	3.12	11.95	11.53	11.02	11.54
	K_2	3.25	2.10	1.25	0.75				
DMF	K_1	6.67	6.21	5.78	5.28	10.50	9.32	7.99	6.88
	K_2	3.20	2.35	1.47	0.95				
Py	K_1	0.53	0.43	0.33	0.25	3.73	2.98	1.43	
	K_2	0.51	0.37	0.17	0.084				
n-$PrNH_2$	K_1	6.96	5.80	4.36	3.64	14.69	12.48	10.83	9.97
	K_2	3.55	2.53	1.95	1.47				
n-$BuNH_2$	K_1	7.0	5.62	4.44	3.46	12.0	10.65	8.53	7.24
	K_2	3.45	2.65	2.05	1.7				
n-$PenNH_2$	K_1	7.04	5.64	4.87	4.22	13.0	10.26	8.34	7.00
	K_2	3.47	2.37	1.70	1.2				
sec-$BuNH_2$	K_1	0.45	0.62	0.75		6.45	5.50	3.73	2.64
	K_2	0.43	0.60	0.79					

[a] Data taken from reference 2.

number (DN) of the coordinating solvent (see Table 4). Although Py is expected to show ligand exchange[2,9] it fits the correlation. Van't Hoff plots (*i.e.*, lnK versus 1/T) of the temperature dependent equilibrium constants exhibit straight lines (r>0.99) (see Figs. 1, 2). The reactions measured with Fa, DMF, $PrNH_2$, n-$BuNH_2$ and n-$PenNH_2$ show a common point of intersection at an isokinetic temperature, T_{iso}, of 285.8 and 281.9K for both K_1 and K_2, respectively. Here Py and *sec*-$BuNH_2$ had to be excluded from the series, the former probably because of its ligand exchange reactions. The latter is hardly coordinated due to steric reasons. Theoretical description of the IKR shows that T_{iso} is associated with a 'resonant' frequency occurring in the far-IR spectra of the reacting system by the relation $\nu_{iso} = kT_{iso}/100hc \approx 0.694^{*}\ T_{iso}$.[13] It is pleasing to note that agreement between

Table 4 Thermodynamic parameters for $[Ni_2(taet)(pmdt)_2](B\phi_4)_2$ and $[Ni(acac)(pmdt)]B\phi_4$ coordinating with different solvents and some aliphatic amines in DCE (ΔH in Kcal mol^{-1}, ΔS in cal $mol^{-1}deg^{-1}$; 1 cal = 4.184 J).

		$[Ni_2(taet)(pmdt)_2(B\phi_4)_2$				$[Ni(acac)(pmdt)]B\phi_4$[a]			
Ligand		K_{298K}	$K_1{*}K_2$	ΔH	ΔS	K_{298K}	ΔH	ΔS	DN
Fa	K_1	4.93	9.07	-4.56	-12.22	11.26	-0.74	-2.32	24.0
	K_2	1.84		-8.65	-28.13				
DMF	K_1	5.99	11.92	-1.36	-1.014	8.16	-2.50	-4.13	26.6
	K_2	1.99		-7.23	-23.11				
Py	K_1	0.368	0.10	-4.47	-16.98	2.56	-8.12	-25.89	33.1
	K_2	0.27		-9.71	-35.6				
n-$PrNH_2$	K_1	5.19	12.35	-3.93	-9.98	9.95	-2.75	-4.71	45.1[b]
	K_2	2.38		-5.12	-15.60				
n-$BuNH_2$	K_1	5.13	12.62	-4.13	-10.71	9.61	-3.05	-5.80	45.9[b]
	K_2	2.46		-4.20	-12.39				
n-$PenNH_2$	K_1	5.44	11.91	-2.97	-6.65	9.65	-3.64	-7.78	45.9[b]
	K_2	2.19		-6.20	-19.42				
sec-$BuNH_2$	K_1	0.616	0.382	+4.37	+13.89	4.56	-5.37	-15.1	45.9[b]
	K_2	0.62		+5.20	+16.68				

[a] Data taken from reference 2. [b] Ref. 7.

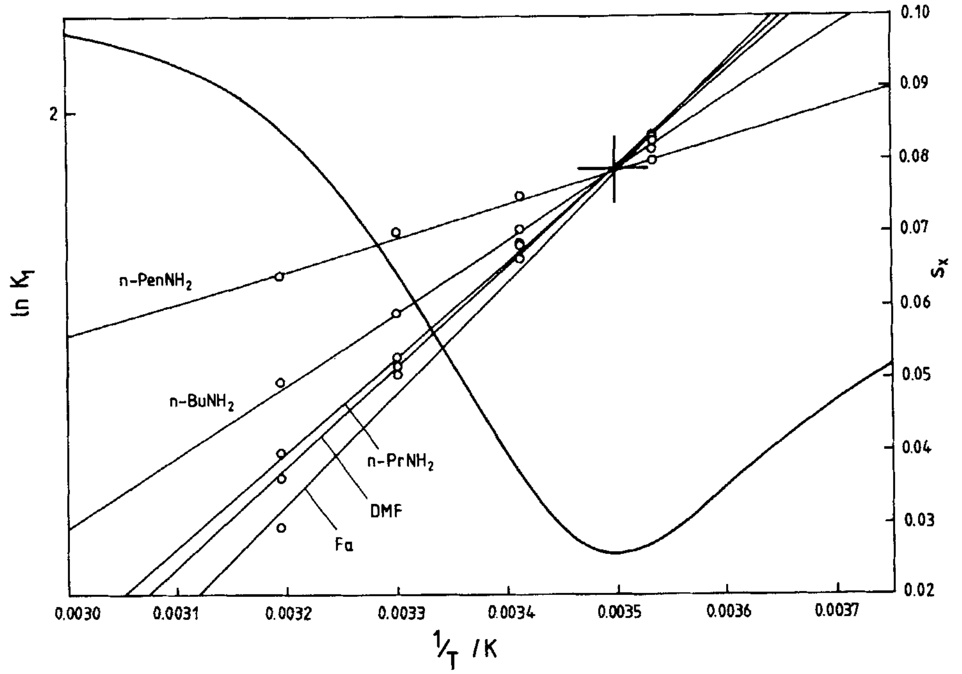


Figure 1 Van't Hoff plot of the formation constant (K_1) of $[Ni_2(taet)(pmdt)_2](B\phi_4)_2$ with different donor solvents in DCE solution.

required and observed absorbance frequencies is in fact found as the IR spectra of the dinuclear five-coordinate Ni(II)-complex show two bands at 203 and 197 cm^{-1}.[13,14]

Thermodynamic data (Table 4) show that the formation of the octahedral species is exothermic. ΔH and ΔS are much smaller than the corresponding values found for $[Ni(acac)(tmen)]^+$, but in general higher than values found for $[Ni(acac)(pmdt)]^+$. The second step of the coordination process has higher values than the first step. The overall ΔH and ΔS values become more negative in the order Py > Fa > $PenNH_2$ > $PrNH_2$ > DMF ≥ $BuNH_2$. The entropic contributions disfavour therefore the coordination of solvent ligands and are more or less compensated by the enthalpy contribution. The different behaviour of *sec*-$BuNH_2$ where the values of logK increase with temperature and their positive enthalpy and entropy changes may be attributed to steric factors.

Statistical factors need to be taken into account. At the first step of coordination, two coordination centers are present in $[Ni_2(taet)(pmdt)_2]^{2+}$ and only one remains in $[Ni_2(taet)(pmdt)_2L]^{2+}$, so that one can expect a ratio for K_1: K_2 of 2:1. To compare the found equilibrium constants with those obtained for the monomeric species, K_2 should be compared with K values for the monomeric five-coordinate species $[Ni(acac)(pmdt)]^+$. They are (with the exception of Py and *sec*-$BuNH_2$) linearly related ($4\ K_{2,\ dimer} = 1.004\ K_{monomer} - 1.29$, $r = 0.98$). This might be explained by consideration of the probability of the formation of $[Ni_2(taet)(pmdt)_2L_2]^{2+}$ from $[Ni_2(taet)(pmdt)_2L]^{2+}$ *via* a simple cross section

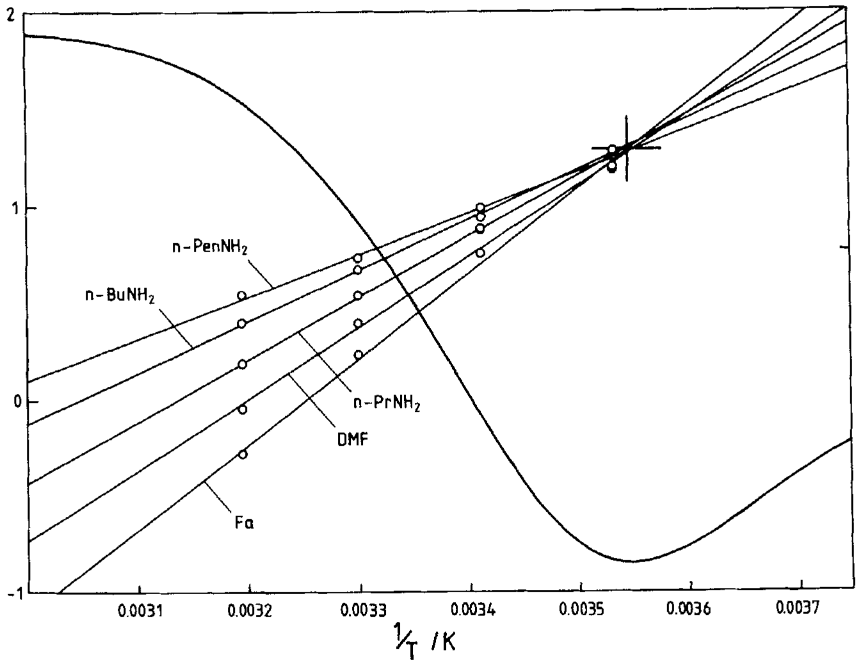


Figure 2 Van't Hoff plot of the formation constant (K_2) for coordination of $[Ni_2(taet)(pmdt)_2](B\phi_4)_2$ with different donor solvents in DCE solution.

model in comparison to the analogue reaction of the monomeric ligand. In this case, doubling the size of the molecule and keeping the reaction centre essentially constant should cause the effective cross-section to be smaller by a factor of 4. The reaction rate for ligand dissociation should be the same for dimeric and monomeric species,[9,11] so that the change in the effective cross-section should be reflected directly in the equilibrium constants and the difference should be entropy controlled. This is confirmed by the experimental data in the neighbourhood of T_{iso} where enthalpic and entropic influences are compensated and the ratio $K:K_1:K_2 \approx 4:2:1$ is observed. The values of $K_1/4$ are in general equal or slightly higher than those of $K_2/2$. The differences increase with increasing temperature, because with increasing distance from the isokinetic point the difference in enthalpic and entropic terms becomes increasingly important. This shows that intramolecular changes in accordance with the bond angle variation rule occur:[12] coordination of the first solvent molecule leads to increasing deformation of the plane around, thus stabilizing five-fold coordination, *i.e.*, decreasing the coordination ability of the second Ni centre towards the second solvent molecule.

The system may be also compared with the mononuclear, square-planar $[Ni(acac)(tmen)]^+$ system. Consecutive coordination of two donor molecules occurs in that case. The addition of the first donor solvent molecule to the square-planar, mononuclear, Ni(II) complex yields a trigonal bipyramid and the second solvent molecule might easily attack the position *cis* to the first.[15] For weak or intermediate donor solvents the coordination of the first donor molecule leads to a square-pyramidal geometry and therefore the second donor molecule easily attacks the *trans* position of the axial ligand (L), *i.e.*, the *cis-trans* mechanism occurs due to different geometrical shapes of the five coordinate species. In the case of the dinuclear complexes, square pyramidal geometry leads to the coordination of the donor solvent opposite to the axial oxygen of the tetraketonate (*trans*-coordination with respect to the axial site) for both nickel(II) centres.

Acknowledgements

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