Thermochemistry of aniline-derivative adducts of nickel(II) acetylacetonate

P.O. Dunstan[*]

Instituto de Química, Universidade Estadual de Campinas, C.P. 6154, CEP 13083-970, Campinas, São Paulo, Brazil

Abstract

The compounds [Ni(acac)$_2$(L)$_2$] (where acac is acetylacetonate and L is aniline (an), 2,6-dimethylaniline (dimean), o- or m-chloroaniline (o- or m-clan)) were synthesized and characterized by melting points, elemental analysis, TG–DTG, and DSC curves and electronic and IR spectroscopy. The enthalpies of dissolution of the adducts, Ni(II) acetylacetonate and ligands in a 1 : 3 (v/v) mixture of aqueous HCl 1.2 M and methanol, were measured and by using thermochemical cycles the following thermochemical parameters for the adducts have been determined: The standard enthalpies for the Lewis acid/base reaction ($\Delta_r H^\theta$), the standard enthalpies of formation ($\Delta_f H^\theta$), the standard enthalpies of decomposition ($\Delta_D H^\theta$), the lattice standard enthalpies ($\Delta_M H^\theta$) and the standard enthalpies of the Lewis acid/base reactions in the gaseous phase ($\Delta_r H^\theta$(g)). The mean standard enthalpies of the nickel–nitrogen bonds have been estimated. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Ni–N bonds; Nickel(II) acetylacetonate adducts; Thermochemical parameters; Thermochemistry

1. Introduction

Adducts of Ni(II) acetylacetonate with heterocyclic bases have been reported and their preparation, characterization and thermochemistry established [1]. Aniline and aniline derivatives are also known to form adducts [2–4]. It is expected that aniline and aniline derivatives will also form coordination compounds with Ni(II) acetylacetonate involving coordination through the nitrogen atom. The substitution of one hydrogen atom in the phenyl group by the electron-withdrawing groups will cause a decrease in the electronic density in the aromatic ring and by an inductive effect, also decrease the electronic density on the nitrogen atom. Similarly the substitution of hydrogen atoms by electron-donating groups should cause an increase in the electronic density in the

aromatic ring and on the nitrogen atom. This paper describes the interaction of Ni(II) acetylacetonate with o- and m-chloroaniline and 2,6-dimethylaniline. Calorimetric measurements were made to determine the mean strength of the Ni–N bonds and study the effect of introducing a chlorine atom or two methyl groups into the phenyl group of aniline.

2. Experimental

2.1. Chemicals

Ni(II) acetylacetonate was prepared by the Charles and Pawlikouski method [5]. The compound was recrystallized from methanol and dehydrated under reduced pressure at 398 K. The product was green and the results of the chemical analysis were: Ni, 22.61; C, 46.09; H, 5.46 mass percent (theoretical: Ni, 22.85; C,

*Tel.: +55-019-7883088; e-mail: dunstan@iqm.unicamp.br

46.75; H, 5.49). Aniline p.a. (Veltec, Química Fin); 2,6-dimethylaniline (99% Aldrich Chemical); o- and m-chloroaniline (98% Aldrich Chemical) were purified by the method of Riddick [6]. Solvents used in the synthesis of adducts were purified by distillation and stored over Linde 4A molecular sieves.

2.2. Analytical

Carbon, hydrogen and nitrogen contents were determined by microanalytical procedures. The nickel content was determined by complexometric titration with 0.01 M EDTA [7] in aqueous solutions of adducts samples. The capillary melting points of the adducts were determined using an UNIMELT equipment from (Thomas Hover).

2.3. Adduct synthesis

The adducts were synthesised by the direct reaction of Ni(II) acetylacetonate with excess of the ligands. A typical procedure is given bellow.

To 1.2 g of Ni(acac)$_2$ (4.7 mmol), 10 ml of aniline was added with stirring. Gently warming dissolves the chelate. The solution was cooled in a freezer for several hours. The solid formed was filtered, washed with three portions of 10 ml of petroleum ether and dried for several hours in vacuo and stored in a desiccator over calcium chloride.

2.4. Infrared spectra

Spectra were obtained with samples in KBr matrix for the adducts. For liquid ligands a film of the ligand sandwiched between NaCl Plates was used. Spectra were recorded with a Perkin Elmer 1600 series FTIR Spectrophotometer in the region 4000–400 cm^{-1}.

2.5. Thermal Studies

TG–DTG and DSC measurements were made in an argon atmosphere in a Du Pont 951 TG Analyser with samples varying in mass from 5.28 to 8.71 mg for TGDTG and from 1.08 to 1.61 for DSC and a heating rate of 10 K min^1 in the temperature ranges 298–1214 K for TG–DTG and 298–673 K for DSC. TG calibration for temperature was made using metallic

aluminium as a standard (mp 660.37°C) and calcium oxalate as a standard for weight calibration. DSC calibration was made using metallic Indium as a standard (mp 156.73°C), $\Delta_s^l H^\theta = 28.4$ Jg^{-1}.

2.6. Calorimetric measurements

All the solution calorimetric determinations were carried out in a LKB 8700-1 precision calorimetric system as described before [8]. The solution calorimetric determinations were performed by dissolving the appropriate mass of samples (14–171 mg) of the adduct or Ni(II) acetylacetonate in a 1 : 3 (v/v) mixture of aqueous HCl 1.2 M and methanol. This mixture was elected because the compounds dissolved quickly and with good thermic effect. The aniline or aniline derivatives were dissolved in this last solution maintaining a molar relation equal to the stoichiometry of the adduct. The accuracy of the calorimeter was checked out by determining the heat of dissolution of tris [(hydroxymethyl)amino methane in 0.1 mol dm^{-3} hydrochloric acid. The result (-29.78 ± 0.03 kJ mol^{-1}) is in agreement with the value recommended by IUPAC [9] (-29.763 ± 0.003 kJ mol^{-1}).

2.7. Electronic spectra

Spectra of the solid adducts in the region 350–2200 nm were obtained with a UV-VIS-NIR Varian-Cary SG Spectrophotometer with a standard reflectance attachment.

3. Results and discussion

All the adducts obtained were solids. The yields range from 27 to 88%. The yields, melting points, colors, appearance and analytical data are summarized in Table 1.

3.1. Infrared Data

The more important i.r. bands are reported in Table 2. Two bands are observed in the region 1600–1500 cm^{-1}. These are assigned to C–O (1604–1589 cm^1) and C–C (1520–1515 cm^{-1}) stretching vibrations [10,11]. The bands observed in

Table 1
Yields in % on preparation, melting points, appearance and analytical data of the adducts

Compound	Yield	M.P. (K)[a]	Appearance	C		H		N		Nickel	
				Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
[Ni(acac)$_2$(an)$_2$]	38	201–204	l.bl.pw	59.62	59.89	6.37	5.93	6.32	6.43	13.25	12.99
[Ni(acsac)$_2$(o-clan)$_2$]	27	158–62	l.bl.pw	51.60	51.53	5.12	4.99	5.47	5.29	11.47	11.44
[Ni(acac)$_2$(m-clan)$_2$]	88	118–20	l.bl.cr	51.60	51.42	5.12	4.91	5.47	5.31	11.47	11.27
[Ni(acac)$_2$(dimean)$_2$]	66	153–4	l.bl.pw	62.55	62.20	7.27	7.22	5.61	5.60	11.76	11.54

[a] Melting with decomposition.
[b] Key: I, light; bl, blue; pw., powder, and cr., crystals.

Table 2
Infrared data for ligands and their complexes (cm^{-1})[a]

| Compound	$\nu_{(C–O)}$	$\nu_{(C–C)}$	$\nu_{(Ni–O)}$	Ligands bands	
				$\nu_{(N–H)}$	$\delta_{(H–N–c)}$
Ni(acac)$_2$	1605 sh	1520 vs	586 m		
an				3437 m, 3354 m	n.o.
[Ni(acac)$_2$(an)$_2$]	1604 vs	1515 vs	574 m	3265 m, 3179 m	n.o.
o-clan				3442 m,3362m	1617 s
[Ni(acac)$_2$(o-clan)$_2$]	1602 vs	1519 vs	573 m	3264 m, 3178 m	n.o.
m-clan				3457 m, 3362 m	1620 s,1597 s
[Ni(acac)$_2$(m-clan)$_2$]	1601 vs	1519 vs	573 m	3256 m, 3167 m	n.o.
dimean				3471m,3386s	1623s
[Ni(acac)$_2$(dimean)$_2$]	1589 vs	1519 vs	570 m	3381 m, 3313 m	n.o.

[a] Key: n.o., not observed.
Intensity of bands: vs, very strong; s, strong; m, medium, and sh, shoulder.

the region 586–570 cm^{-1} are assigned to Ni–O modes [12–15]. No bands could reasonably be assigned to the stretching vibration of Ni–N bond. It has been observed in related adducts of Co(II), Ni(II) and Zn(II) that it lies bellow 200 cm^{-1} [12] due to the low free energy change accompanying adduct formation, that is only of about −1.5 kcal mol^{-1} for Co(II) acetyl-acetonate [12]. The shifts to lower frequencies observed in the adducts of $\nu_{(CO)}$; $\nu_{(CC)}$ and $\nu_{(NiO)}$ relative to the free Ni(II) acetylacetonate, indicated that the amines were coordinated to the nickel ion [16]. Big shifts to lower frequencies of $\nu_{(N–H)}$ of ligands after coordination were also observed, indicating coordination of ligands through the nitrogen atom of the NH group [17,18].

3.2. Thermal studies

TG–DTG studies show that the adducts followed different processes of thermal dissociation:

1. [Ni(acac)$_2$(an)$_2$] → [Ni(acac)$_2$an] + an
   [Ni(acac)$_2$an] → Ni(acac)$_2$ + an
   Ni(acac)$_2$ → pyrolysis

2. [Ni(acac)$_2$ (o-clan)$_2$] → [Ni(acac)$_2$(o-clan)$_{,1.5}$] + 0.5(o-clan)

   [Ni(acac)$_2$ (o-clan)$_{1.5}$] → [Ni(acac)$_2$(o-clan)$_{05}$] + (o-clan)
   [Ni(acac)$_2$. (o-clan)$_{05}$] → Ni(acac)$_2$ + 0.5 (o-clan)
   Ni(acac)$_2$ → pyrolysis

3. [Ni(acac)$_2$(m-clan)$_2$] → [Ni(acac)$_2$(m-clan)$_{1.5}$] + 0.5 (m-clan)

   [Ni(acac)$_2$(m-clan)$_{1.5}$] → [Ni(acac)$_2$(m-clan)$_{075}$] + 0.75 (m-clan)
   [Ni(acac)$_2$(m-clan)$_{0.75}$] → 0.75(m-clan) + pyrolysis Ni(acac)$_2$

4. [Ni(acac)$_2$(dimean)$_2$] → [Ni(acac)$_2$(dimean)$_{0.25}$] - + 1.75 dimean

[Ni(acac)$_2$(dimean)$_{025}$] → 0.25 dimean + pyrolysis Ni(acac)$_2$
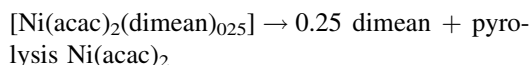
The DSC curves of the adducts are consistent with TG–DTG data. They present several endothermic peaks due to the elimination of ligand, elimination of ligand with melting, elimination of ligand with pyrolysis of Ni(AcAc)$_2$ and decomposition of the product of the pyrolysis of Ni(acac)$_2$. The Table 3 lists the thermoanalytical data of the adducts.

3.3. Electronic spectra

Table 4 presents the band maxima assignments and calculated ligand field parameters for the adducts. The ligand field parameters were calculated according to Reedijk et al. [19]. The electronic spectra of the adducts present four absorption bands: ν_1 in the region 10469–12740 cm^{-1}; ν_2 in the region 16465–16720 cm^{-1} and ν_3 in the region 27742–29677 cm^{-1}. ν_4 in the region 12778–12958 cm^{-1}

were observed for some adducts. According to the number and position of these bands and considering the magnitude of the crystal field parameters as compared with that of Bolster [20] we can conclude that the Ni(Il) ion is pseudo-octahedrally surrounded by two nitrogen atoms and four oxygen atoms. Pseudo-octahedral complexes of Ni(II) have been widely studied by Reedijk et al. [19]. They concluded that the ligand-field O$_h$ is a good approaching for these pseudo-octahedral complexes. The crystal field parameters obtained for the compounds [Ni(acac)$_2$L$_2$] are in agreement with these results.

3.4. Calorimetric measurements

The standard enthalpies of dissolution of Ni(II) acetylactonate, ligands and adducts were obtained as previously described [1]. Ni(acac)$_2$ exists as a trimeric structure in the solid state [21]. Thus a hypothetical monomer for the calculation of the standard enthalpy of dissolution of Ni(acac)$_2$ had to be

Table 3
Thermoanalytical data of the compounds

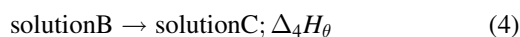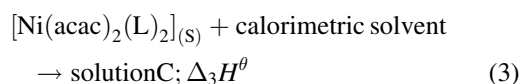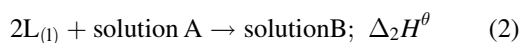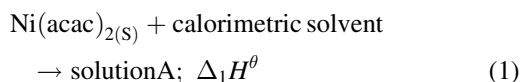| Compound	% Mass lost		TG temperature range (K)	Species lost	DSC peak temperature (K)	Enthalpy (kg/mol^{-1})
	Calcd.	Obs.				
[NI(acac)$_2$(an)$_2$]	21.01	20.96	455–662	-an	402	69.6
	21.01	23.04	662–459	-an	473	100.1
		50.12	459–634	-Ni(acac)$_2$[a]	563	24.8
		3.65	634–689		671	6.0
		2.23[b]				
Ni(acac)$_2$(o-clan)$_2$]	12.46	16.80	380–416	−0.5(o-clan)	397	26.9
	24.91	22.00	416–467	-(o-clan)	438	31.5
	12.46	13.40	467–532	−0.5(o-clan)	492	47.5
	50.18	25.80	532–607	-Ni(acac)$_2$[a]	662	14.0
		13.54	607–608			
		6.53[b]				
[Ni (acac)$_2$ (m-clan)$_2$]	12.46	11.07	306–378	−0.5(m-clan)	393	28.1
	18.68	17.51	378–409	−0.7(m-clan)	489	73.8
	68.84	34.28	409–479	−0.75(m-Ni(acac)$_2$[a]	630	16.4
		30.71	479–592			
		4.46	592–677			
		2.27[b]				
[Ni (acac)$_2$ (dimean)$_2$]	42.47	41.09	322–426	−1.75 dimean	429	69.7
	57.53	51.23	426–641	−0.25 dimean- Ni(acac)$_2$[a]	531	27.1
		4.69	641–700		659	77.9
		2.99[b]				

[a] Pyrolysis of Ni(acac)$_2$.
[b] Residue at 1273 K.

Table 4
Band maximum assignments and calculated ligand-field parameters for the compounds

Compound	ν_1/cm^{-1}	ν_4/cm^{-1}	ν_2/cm^{-1}	ν_3/cm^{-1}	Dq/cm^{-1}	B/cm^{-1}	Dq/B	β^*
[Ni(acac)$_2$(an)$_2$]	10174	12845	16465	29.677	1017	914	1.11	0.89
[Ni(acac)$_2$(o-clan)$_2$]	10251	12778	16545	27879	1025	871	1.18	0.85
[Ni(acac)$_2$ (m-clan$_2$)]	10470	12958	16692	27742	1047	818	1.28	0.79
[Ni(acac)$_2$ (dimen)$_2$]	10226	12453	16720	28527	1023	958	1.07	0.93

$\nu_1 =^3 T_{2g} \leftarrow^3 A_{2g}$, $\nu_4 =^1 E_g \leftarrow^3 A_{2g}$, $\nu_2 =^3 T_{1g}(F) \leftarrow^3 A_{2g}$, $\nu_3 =^3 T_{1g}(P) \leftarrow^3 A_{2g}$ $\beta^+ = B/Bo$, $Bo = 1030\ cm^{-1}$ (Ni^{2+}).

assumed. The standard enthalpies of dissolution were obtained according with the standard enthalpies of reactions 1–4 in solution:

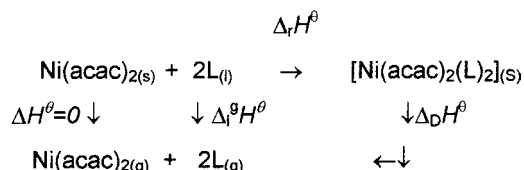$$Ni(acac)_{2(S)} + \text{calorimetric solvent}$$
$$\rightarrow \text{solution A}; \ \Delta_1 H^\theta \quad (1)$$

$$2L_{(I)} + \text{solution A} \rightarrow \text{solution B}; \ \Delta_2 H^\theta \quad (2)$$

$$[Ni(acac)_2(L)_2]_{(S)} + \text{calorimetric solvent}$$
$$\rightarrow \text{solution C}; \Delta_3 H^\theta \quad (3)$$

$$\text{solution B} \rightarrow \text{solution C}; \Delta_4 H_\theta \quad (4)$$

The application of Hess'law to the series of reactions Eqs. (1)–(4) gives the standard enthalpies of the acid/base reactions ($\Delta_m H\%$), according to the reaction Eq. (5):

$$Ni(acac)_2 + 2L \rightarrow [Ni(acac)_2 L_2];$$
$$\Delta_m \Delta_1 H^\theta + \Delta_2 H^\theta - \Delta_3 H^\theta, \quad (5)$$
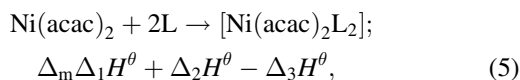
since the final B and C solutions are equivalent and $\Delta_4 H^\theta = 0$. Table 5 gives the values obtained for the enthalpies of dissolution of Ni(II) acetylacetonate ($\Delta_1 H^\theta$), ligands into the solution of Ni(acac)$_2$

($\Delta_2 H^\theta$) and of the adducts ($\Delta_3 H^\theta$). Uncertainty intervals given in this table are twice the standard deviations of the means of about five replicate measurements on each compound. Combined errors were calculated from the square root of the sum of the square of the component errors.

From the values obtained for the standard enthalpies of the acid/base reactions and using appropriate thermochemical cycles [22,23], the following thermochemical parameters were determined: the standard enthalpies of formation ($\Delta_f H^\theta$), being equal to $\Delta_f H^\theta(\text{adduct}_{(s)}) = \Delta_r H^\theta + \Delta_f H^\theta$ (Ni(acac)$_{2(s)}$)+2 $\Delta_f H^\theta$(ligand$_{(I)}$); the standard enthalpies of decomposition ($\Delta_D H^\theta$), from the cycle

$$\Delta_r H^\theta$$
$$Ni(acac)_{2(s)} + 2L_{(l)} \rightarrow [Ni(acac)_2(L)_2]_{(S)}$$
$$\Delta H^\theta=0 \downarrow \qquad \downarrow \Delta_l^g H^\theta \qquad \downarrow \Delta_D H^\theta$$
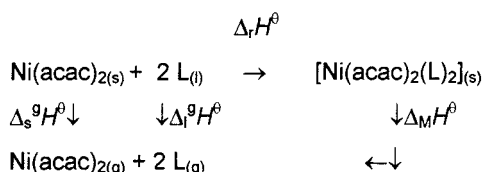$$Ni(acac)_{2(g)} + 2L_{(g)} \qquad \leftarrow \downarrow$$

being equal to

$$\Delta_D H^\theta = 2\Delta_l^g H^\theta - \Delta_r H^\theta,$$

the standard lattice enthalpies ($\Delta_M H^\theta$), from the cycle

Table 5
Enthalpies of dissolution at 298.15 K

Compound	Calorimetric solvent[a]	Number of experiments	$\Delta_i H^\circ/kJ\ mol^{-1}$
Ni(acac)$_2$	HCl 1.2M–methanol	19	($i = 1$) −3.73 ± 0.13
an	2:1 Ni(acac)$_2$–HCl 1.2M–methanol	5	($i = 2$) −50.39 ± 0.42
[Ni(acac)$_2$(an)$_2$]	HCl 1.2M–methanol	5	($i = 3$) 3.51 ± 0.18
o-clan	2:1 Ni(acac)$_2$–HCl 1.2M–methanol	4	($i = 2$) −29.67 ± 0.29
[Ni(acac)$_2$(o-clan)$_2$]	HCl 1.2M–methanol	4	($i = 3$) −18.96 ± 0.36
m-clan	2:1 Ni(acac)$_2$–HCl 1.2M–methanol	6	($i = 2$) −36.05 ± 0.58
[Ni(acac)$_2$(m-clan)$_2$]	HCl 1.2M–methanol	4	($i = 3$) −3.31 ± 0.06
dimean	2:1 Ni(acac)$_2$–HCl1:2M–methanol	5	($i = 2$) −41.84 ± 1.12
[Ni(acac)$_2$ (dimean)$_2$]	HCl 1.2M–methanol	4	($i = 3$) 2.40 ± 0.11

[a] 1 : 3 mixture of 1.2 mol l^{-1} aqueous hydrochloric acid and methanol.

$$\Delta_r H^\theta$$

Ni(acac)$_{2(s)}$ + 2 L$_{(l)}$ → [Ni(acac)$_2$(L)$_2$]$_{(s)}$

$\Delta_s{}^g H^\theta\downarrow$ $\downarrow\Delta_l{}^g H^\theta$ $\downarrow\Delta_M H^\theta$

Ni(acac)$_{2(g)}$ + 2 L$_{(g)}$ ←↓

being equal to

$$\Delta_M H^\theta = \Delta_r H^\theta - \Delta_s^g H^\theta - 2\Delta_l^g H^\theta$$

and the standard enthalpies of the Lewis acid/base reactions in the gaseous phase ($\Delta_r H^\theta$(g)), from the cycle

$$\Delta_r H^\theta(g)$$

Ni(acac)$_{2(g)}$ + 2 L$_{(g)}$ → [Ni(acac)$_2$(L)$_2$]$_{(g)}$

$\Delta_s{}^g H^\theta\uparrow$ $\uparrow\Delta_l{}_H{}^\theta$ $\uparrow\Delta_s{}^g H^\theta$

$$\Delta_r H^\theta$$

Ni(acac)$_{2(S)}$ + 2 L$_{(l)}$ → [Ni(acac)$_2$(L)$_2$]$_{(s)}$
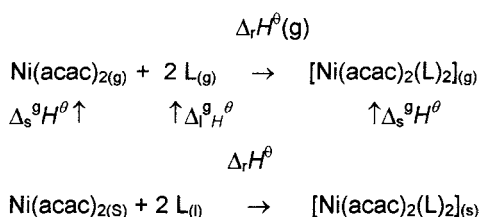
Being equal to $\Delta_r H^\theta(g) = -\Delta_s^g H^\theta - 2\Delta_l^g H^\theta + \Delta_r H^\theta + \Delta_s^g H^\theta$ These last values can be used to calculate the standard enthalpies of the Ni–N bonds [23], being equal to $\bar{D}$(Ni–N)$=-\Delta_r H^\theta$(g)/2. Table 6 lists the values obtained for all these thermochemical parameters for the adducts. For the determination of ($\Delta_r H^\theta$(g)) it was necessary to assume that the molar standard enthalpy of sublimation of each adduct was equal to the enthalpy of sublimation or vaporization of one mole of ligand [22,23,26,27], as melting points and thermal studies showed that the adducts decomposed on heating and were not found in the liquid phase and probably not in the gaseous phase.

Based on the $\Delta_r H^\theta$ values for the adducts of the same stoichiometry we obtain the basicity sequence: o-clan > an > dimean > m-clan. Using the $\bar{D}$ (Ni–N) values we obtain the sequence o-clan > dimean > an > m-clan. The expected order would be dimean > an > m-clan ≈ o-clan, due to an inductive effect of substitution of one hydrogen atom in the phenyl group of an by the electron withdrawing chlorine atom in o- or m-clan. dimean is expected to be a stronger base than an as two hydrogen atoms of the phenyl group of an are substituted by two electron-donating methyl groups. This leads to the decrease of the electronic density available for bonding on the nitrogen atom in the first case and to the increase of that in the last case. The same expected order is observed on the basis of $\bar{D}$(Ni–N) values with the exception of the position of o-clan. This could be due to the contribution of another kind of interaction like intramolecular hydrogen bonding between nitrogen and chlorine atoms in o-clan.

Comparing the ligand field parameters Dq with the thermochemical parameters $\bar{D}$(Ni–N) for the adducts of an, m-clan and dimean, we observed that the Dq values decrease with the increase of $\bar{D}$ (Ni–N) values indicating that the splitting of the d orbitals of Ni(II) ion is not favored by stronger Ni–N bonds (Fig. 1). The contrary was observed for Ni(II) acetylacetonate adducts with heterocyclic bases [1]. Comparing β^+ values with $\bar{D}$(Ni–N) values we observed for the same adducts, that the β^+ values increase with the increase of $\bar{D}$(Ni–N) values, indicating that the covalence of the d orbitals of Ni(II) ion is lower as the Ni–N bond is stronger (Fig. 2). This is also the contrary of the

Table 6
Summary of the thermochemical results (kJ mol^{-1})

| Compound	$\Delta_r H^\theta$	$\Delta_f H^\theta$	Δ_s^g ($H^\theta/\Delta_\ell^g H^\theta$)	$\Delta_M H^\theta$	$\Delta_D H^\theta$	$\Delta_r H^\theta$(g)	$\bar{D}$ (Ni–N)
Ni(acac)$_{2(s)}$		-910.6 ± 2.1[a]	95.4[a]				
an$_{(l)}$		31.03 ± 0.70[b]	55.8 ± 1.06[b]				
o-clan$_{(l)}$		-6.8[c]	62.2[c]				
m-clan$_{(l)}$		-11.8[c]	61.9[c]				
dimean$_{(l)}$		-45.1[c]	66.9[c]				
[Ni(acac)$_2$(an)$_2$]$_{(s)}$	-50.61 ± 0.48	-899.2 ± 2.3		-257.6 ± 2.4	162.2 ± 2.1	-201.8 ± 2.6	100.9 ± 1.3
[Ni(acac)$_2$(o-clan)$_2$]$_{(s)}$	-52.36 ± 0.48	-949.4 ± 2.9		-272.2 ± 2.3	176.8 ± 2.1	$-210,0 \pm 2.5$	105.0 ± 1.3
[Ni(acac)$_2$(m-clan)$_2$]$_{(s)}$	-36.47 ± 0.60	-970.7 ± 4.6		-255.7 ± 4.2	160.3 ± 4.0	-193.8 ± 4.6	96.9 ± 2.3
[Ni(acac)$_2$(dimean)$_2$]$_{(s)}$	-43.17 ± 1.15	-1044.0 ± 3.1		-272.4 ± 4.3	177.0 ± 4.2	-205.5 ± 4.7	102.8 ± 2.4

[a] Reference [24].
[b] Reference [25].
[c] Reference [1].
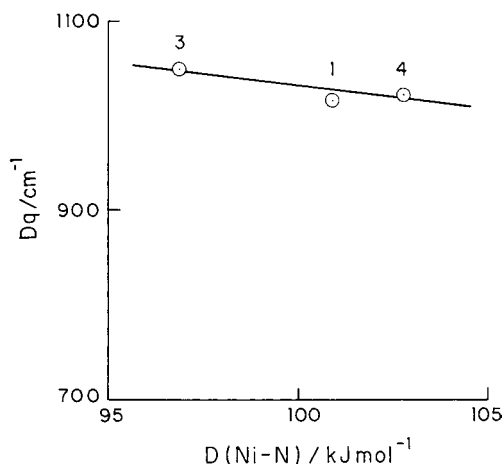
Fig. 1. Correlation of Dq values with $\bar{D}$(Ni–N) values for the adducts of Ni(acac)$_2$ with (1) an, (3) m-clan and (4) dimean.

observation for Ni(ll) acetylacetonate adducts of heterocyclic bases [1]. Thus the π-basicity of aniline and derivatives increase in the sequence: m-clan < an < -dimean (Fig. 1) and the π-acidity of heterocyclic bases
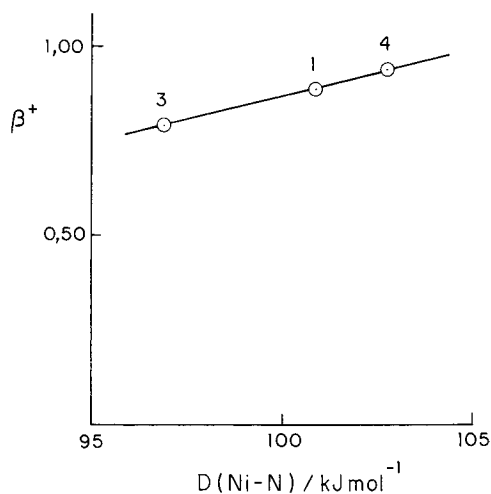
increase in the sequence:py < β-pico < pipd < 3-cyanopy [1], whereas the Ni–N bonds become stronger.

References

[1] P.O. Dunstan, Thermochim. Acta 317 (1998) 165.
[2] E. Montignie, Bull. Soc. Chim. Fr. 5 (1935) 1365.
[3] T. Okuda, S. Gimar, H. Ishihara, H. Negita, J. Mol. Struct. 81 (1982) 261.
[4] P.O. Dunstan, J. Chem. Eng. Data 39 (1994) 667.
[5] R.G. Charles, M.A. Pawlikowski, J. Phys. Chem. 62 (1958) 440.
[6] J.A. Riddick, W.B. Bunger, Organic Solvents, 3rd ed., Wiley, New York, 1970, p. 815.
[7] H.A. Flaschka, EDTA Titrations: An Introduction To Theory and Practice, Pergamon Press, London, 1964, p. 83.
[8] P.O. Dunstan, Thermochim. Acta 197 (1992) 201.
[9] E.F. Henrigton, Pure Appl. Chem. 40 (1974) 391.
[10] S. Pinchas, B.L. Silver, I. Laulicht, J. Chem. Phys. 46 (1967) 1506.
[11] G.T. Bennke, K. Nakamoto, Inorg. Chem. 6 (1967) 443.
[12] J.N. Haigh, N.P. Slabbert, D.A. Thornton, J. Inorg. Nucl. Chem. 32 (1970) 3635.
[13] G. Marcotrigiano, R. Battistuzzi, G.C. Pellacani, Can. J. Chem. 50 (1972) 2559.
[14] R.D. Hancock, D.A. Thornton, J. Molec. Struct. 4 (1969) 361.
[15] K. Nakamoto, P.J. Carthy, A.E. Martell, J. Am. Chem. Soc. 83 (1961) 1272.
[16] D.P. Graddon, R.A. Schulz, Aust. J. Chem. 18 (1965) 1731.
[17] I.S. Ahuja, Inorg. Chim. Acta 3 (1969) 110.
[18] I.S. Ahuja, A. Garg, Inorg. Nucl. Chem. Letters 7 (1971) 937.
[19] J. Reedijk, P.W.N.M. van Leeuwen, W.L. Croeneveld, Recueil 87 (1968) 87.
[20] M.W.G. Bolster, The coordination chemistry of aminophosphine oxides and related compounds, Thesis Leiden, 1972 p. 89.
[21] A.P. Ginsberg, R.L. Martin, R.C. Sherwood, Inorg. Chem 7 (1968) 932.
[22] P.O. Dunstan, Thermochim. Acta 197 (1992) 201.
[23] P.O. Dunstan, R.C.R. dos Santos, Thermochim. Acta 156 (1989) 163.
[24] W. Wladylaw, E. Giera, J. Chem. Thermodynamics 15 (1983) 203.
[25] J.B. Pedley, J. Rylance, Sussex – N.P.L. Computer Analysed Thermochemical Data: Organic and Organometallic Compounds, Sussex University, Brighton, England, 1970.
[26] P.O. Dunstan, Thermochim. Acta 240 (1994) 91.
[27] A.P. Chagas, C. Airoldi, Polyhedron 8 (1989) 1093.

Fig. 2. Correlation of β^+ values with $\bar{D}$(Ni–N) values for the adducts of Ni(acac)$_2$ with (1) an, (3) m-clan and (4) dimean.