

Thermochemistry of adducts of nickel(II) acetylacetonate chelate with heterocyclic bases

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Abstract

The compounds $\text{Ni}(\text{AcAc})_2 \cdot n\text{L}$ (where AcAc is acetylacetonate; L piperazine (pipz), morpholine (morph), piperidine (pipd), pyridine (py), 3-methylpyridine (β -pico), 4-methylpyridine (γ -pico), 3-cyanopyridine (3-cyanopy), 4-cyanopyridine (4-cyanopy), 2,2'-bipyridine (bipy) or quinoline (quin), and $n=1$ or 2) were synthesized and characterized by elemental analysis, melting points, thermal studies and electronic and IR spectroscopy. The enthalpies of dissolution of adducts, Ni(II) chelate and ligands in 25% (v/v) aqueous HCl 1.2 N in 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 ($\Delta_r H^\theta(\text{g})$). The mean standard enthalpies of the nickel–nitrogen bonds have been estimated. © 1998 Elsevier Science B.V.

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1. Introduction

Numerous complexes of β -diketone chelates of divalent 3d-electron elements with several heterocyclic bases are reported in the literature [1–15]. However, there is a lack of information about the enthalpies of the transition-element–nitrogen bonds in these kind of compounds. Adducts of Ni(II) acetylacetonate chelate with heterocyclic bases were synthesized with the intention of getting the enthalpies involved in the formation of these adducts and establishing correlations between the bond energies and other thermochemical parameters. It is possible that correlations between ligand field parameters of the adducts and

their thermochemical parameters exist. Inductive effects on the energy of the Ni(II)–N bonds due to substitution of one hydrogen atom of the pyridine ring by the electronic donor methyl group or the electronic withdrawing cyano group, or the substitution of one carbon atom in the piperidine ring by the more electronegative nitrogen or oxygen atoms, were also studied.

2. Experimental

2.1. Chemicals

Ni(II) acetylacetonate was prepared by the Charles and Pawlikowski method [16]. The compound was recrystallized from methanol and dehydrated under

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reduced pressure at 398 K. The quelate was green and the results of the elemental analysis were: Ni, 22.61; C, 46.29; H, 5.46 mass percent (theoretical: Ni, 22.85; C, 46.75; H, 5.49). Piperazine (99%, Aldrich) was purified by recrystallization from methanol (m.p. 107–108°C). Morpholine (99% A.C.S. Aldrich), pyridine (A.C.S. Reagen), 3-methylpyridine (p.a. Baker), quinoline (98%, Aldrich) and piperidine (99%, RPE Analyticals, Carlo Erba), were all purified by distillation using an efficient column and stored over 4 Å molecular sieves (b.p. obtained 123–124, 111–112, 139–140, 140–141, 111–112/20 mmHg and 103–104°C, respectively). 2,2'-Bipyridine (99%, Aldrich) was purified by recrystallization from ethanol according to the method described by Gallagher et al. [17] (m.p. 193–194°C). 3-Cyanopyridine (98%, Aldrich) and 4-cyanopyridine (98%, Aldrich) were purified by recrystallization from methanol (m.p. 46–50 and 77–80°C, respectively). Other solvents used in the synthesis of the adducts were purified by distillation and stored over Linde 4 Å 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 solution [18] of the aqueous solution of adducts samples. The capillary melting points of the adducts were determined using and UNIMELT equipment from Thomas Hover.

2.3. Adduct synthesis

The adducts were synthesized by the reaction of Ni(II) acetylacetonate and ligands in solution.

To a solution of 1.2 g of Ni(AcAc)₂ (4.7 mmol) in 80 ml of hot methanol, 0.97 g of 3-cyanopyridine dissolved in 10 ml of hot methanol was added slowly, dropwise with stirring. The volume was reduced to 30–40 ml and the mixture cooled in an ice bath. The solid formed was filtered, washed with three portions of 10 ml of petroleum ether and dried for several hours in vacuo. The product was stored in a desiccator over calcium chloride. Nearly all the adducts were prepared using a donor/acceptor molar ratio of 2/1. Only in the case of piperidine an excess of ligand was used. In all cases, methanol was used as a solvent for dissolving

Ni(AcAc)₂ and petroleum ether was used as a solvent for washing. In the cases of liquid ligands, they were added directly to the solution of Ni(AcAc)₂.

2.4. Infrared spectra

Spectra were obtained with samples in KBr matrix for adducts and solid ligands. For liquid ligands a film of the ligand sandwiched between NaCl plates was used. A Perkin-Elmer 1600 series FTIR spectrophotometer in the 4000–400 cm⁻¹ region was used.

2.5. Thermal studies

TG and DSC measurements were obtained in an argon atmosphere in a Du Pont 951 TG analyser with samples varying in mass from 8.28 to 13.14 mg (DSC) and from 9.33 to 14.80 mg (TG-DTG) and a heating rate of 10 K min⁻¹ in the 298–673 K (DSC) and 298–1214 K (TG-DTG) temperature ranges. TG calibration for temperature was made using metallic aluminium as a standard (m.p. 660.37°C) and calibration for weight was carried out by using calcium oxalate as a standard. DSC calibration was made using metallic indium as a standard (m.p. 165.73°C, $\Delta_s^1 H^\theta = 28.4 \text{ J g}^{-1}$).

2.6. Calorimetric measurements

All the calorimetric determinations of the solution were carried out in an LKB 8700-1 precision calorimeter as described before [19]. The solution calorimeter measurements were performed by dissolving samples of 5–92 mg of the adduct or Ni(II) acetylacetonate in 100 ml of 25% (v/v) 1.2 N HCl in methanol and the ligand 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 HCl. The result ($-29.78 \pm 0.03 \text{ kJ mol}^{-1}$) is in agreement with the value recommended by IUPAC [20] ($-29.763 \pm 0.003 \text{ kJ mol}^{-1}$).

2.7. Electronic spectra

Spectra of the solid adducts in the region 350–2200 nm were obtained with a UV-VIS NIR Varian-

Cary 5G spectrophotometer with a standard reflectance attachment.

3. Results and discussion

All the adducts obtained were solids. The yields range from 45 to 88%. The yields, melting points, colours, appearance and analytical data are summarized in Table 1.

3.1. Infrared data

The more important IR bands are reported in Table 2. The assignments of $\nu_{(C-C)}$ in the 1600–1500 cm^{-1} region are based on the works of Pinchas et al. [21] and Bennke and Nakamoto [22]. Two bands are observed in this region for the adducts. These bands are assigned to C–C (1602–1587 cm^{-1}) and C–C (1520–1513 cm^{-1}) stretching vibrations. The bands in the 600–400 cm^{-1} region are assigned to Ni–O modes [3,6,23,24]. The $\nu_{(C-O)}$, $\nu_{(C-C)}$ and $\nu_{(Ni-O)}$ bands shift to lower frequencies in the adducts relative to the uncoordinated Ni(II) acetylacetonate, thus indicating that the amines were bonded to the nickel ion. These shifts are much more marked than those observed for the formation of Ni(II) acetylacetonate chelate [9]. Considerable shifts to lower frequencies of the $\nu_{(N-H)}$ bands of ligand after coordination are also observed. This is indicative of coordination of piperazine, morpholine and piperidine through the nitrogen

atom of their NH group [25,26]. In the morpholine adduct, the positive shift of C–O–C stretching vibration with respect to free morpholine excludes the possibility of oxygen-to-nickel coordination [25]. The change observed in the H–N–C deformation region (889–815 cm^{-1}) also affords evidence of the coordination of the nitrogen atom of ligands [27]. The coordinated pyridine is distinguished from free pyridine by the presence in the adduct of a weak band at 1214 cm^{-1} and by the dislocation of bands at 1573, 584 and 431 cm^{-1} in free pyridine [28] to higher frequencies. The last band was observed but two of the other bands were overlapped by vibrations of the Ni(II) chelate in the same region. The infrared spectra of β - or α -pico adducts show appreciable dislocations towards higher frequencies of the bands at 1585–1545 and 1206 cm^{-1} in the ligands [29],[30]. Only the dislocation of the last band is observed, the other two bands being covered by Ni(II) acetylacetonate bands. For 3- and 4-cyanopyridine adducts this last band is observed at 1257–1256 cm^{-1} (1216–1216 cm^{-1} in three ligands). The infrared data can be interpreted in terms of coordination of these ligand through the heterocyclic nitrogen atom to the nickel ion [28–30]. The infrared spectra of the bipy adduct shows the appearance of new bands after coordination. Two new bands appear at 1350 and 830 cm^{-1} , both of which are absent in free bipy and are due to adduct formation [31]. The infrared spectra of the quin adduct show dislocation of several bands with respect to the ligand [4]. A new band is observed at 1260 cm^{-1} after

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

Compound	Yield	Melting point ^a /K	Appearance ^b	C		H		N		Ni	
				cal.	found	cal.	found	cal.	found	cal.	found
Ni(AcAc) ₂ -pipz	73	310–312	1.bl.cr	49.02	49.01	7.05	7.22	8.17	8.28	17.11	16.99
Ni(AcAc) ₂ -2 morph	74	205–206	1.bl.cr	50.14	49.93	7.48	7.50	6.50	6.39	13.62	13.53
Ni(AcAc) ₂ -2 pipd	45	184–185	1.bl.cr	56.23	55.98	8.49	8.64	6.56	6.52	13.74	13.50
Ni(AcAc) ₂ -2 py	57	184–186	bl.cr	57.87	57.86	5.83	5.93	6.75	6.79	14.14	13.98
Ni(AcAc) ₂ -(β -pico)	63	185–186	1.pu.cr.	59.62	59.84	6.37	6.25	6.32	6.33	13.25	13.19
Ni(AcAc) ₂ -(γ -pico)	58	185	bl.cr.	59.62	59.27	6.37	6.29	6.32	6.05	13.25	13.26
Ni(AcAc) ₂ -(3-cyanopy) ₂	83	210–211	1.pu.cr	56.81	56.97	4.77	4.50	12.04	12.10	12.62	12.40
Ni(AcAc) ₂ -(4-cyanopy) ₂	74	233–235	1.gr.cr	59.81	56.86	4.77	4.58	12.04	12.13	12.62	12.64
Ni(AcAc) ₂ -bipy	88	232	1.gr.cr.	58.15	58.34	5.37	5.09	6.78	6.86	14.21	14.31
Ni(AcAc) ₂ -2 quim	75	210–211	1.bl.cr	65.27	65.07	5.48	5.28	5.44	5.33	11.39	11.36

^a Melting with decomposition.

^b Key: l, light; bl, blue; pu, purple; gr, green; cr, crystals.

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

Compound	Ligand bands										new bands	
	$\nu(\text{C-O})$	$\nu(\text{C-C})$	$\nu(\text{Ni-O})$	$\nu(\text{N-H})$	$\nu(\text{C-C})$	$\nu(\text{C-N})$	ring	$\nu(\text{C-O-C})$	$\delta(\text{H-N-C})$	$\alpha(\text{C-C-C})$		$\theta(\text{O-C})$
Ni(AcAc) ₂	1593vs	1520vs	586m									
pipz				3328m	1461s				861m, 815s			
Ni(AcAc) ₂ :pipz	1589vs	1514vs	573m, 416m	3256m					873s			
morph				3320m	1452s			1097s	889m, 835s			
Ni(AcAc) ₂ :2morph	1590vs	1513vs	567m, 416m	3267m				1107s	878s, 765m			
pipd				3276m	1467s				860s, 825m			
Ni(AcAc) ₂ :2pipd	1602vs	1515vs	568m, 416m	3227m					872s			
py					1573sh					584 s	431 m	
Ni(AcAc) ₂ :2py	1587vs	1518vs	574s, 418s	n.o.	n.o.					n.o.	437 s	1214w
β -pico					1572sh, 1558s							
Ni(AcAc) ₂ :(β -pico) ₂	1595vs	1515vs	574s, 413s		1585s, 545s							
γ -pico												
Ni(AcAc) ₂ :(γ -pico) ₂	1593vs	1517vs	495m, 418m									
3-cyanopy								2231s	1219s			
Ni(AcAc) ₂ :3-cyanopy) ₂	1591vs	1516vs	581m, 419s					2234s	1256m			
4-cyanopy								2236s	1216s			
Ni(AcAc) ₂ :4-cyanopy) ₂	1591vs	1514vs	562s, 420s					2236s	1257m			
bipy					1576s				990m		75vs	
Ni(AcAc) ₂ :bipy	1594vs	1513vs	566m, 409m	n.o.				n.o.			n.o.	1359m, 830w
quin					1602s				1031m			
Ni(AcAc) ₂ :2quin	1592vs	1519vs	488m, 420m		n.o.				n.o.			1260m

^a Key: α , ring deformation in plane; θ , ring deformation out of plane; ν , stretching; δ , angular deformation; ring, ring breathing; n.o., not observed. Intensity of band: vs, very strong; s, strong; m, medium; w, weak; and sh, shoulder.

coordination. The infrared data of the bipy and quin adducts can be interpreted in terms of coordination of these ligands through the nitrogen atom to the nickel ion [4],[31]

3.2. Thermal studies

Thermogravimetry and derivative thermogravimetry of the adducts show that the thermal dissociation process of the adducts were of different types:

- I. $\text{Ni}(\text{AcAc})_2 \cdot 2\text{L} \rightarrow \text{Ni}(\text{AcAc})_2 \cdot 1.3\text{L} + 0.7\text{L}$
 $\text{Ni}(\text{AcAc})_2 \cdot 1.3\text{L} \rightarrow \text{pyrolysis}$
- II. $\text{Ni}(\text{AcAc})_2 \cdot 2\text{L} \rightarrow \text{Ni}(\text{AcAc})_2 \cdot \text{L} + \text{L}$
 $\text{Ni}(\text{AcAc})_2 \cdot \text{L} \rightarrow \text{pyrolysis}$
- III. $\text{Ni}(\text{AcAc})_2 \cdot 2\text{L} \rightarrow \text{Ni}(\text{AcAc})_2 \cdot \text{L} + \text{L}$
 $\text{Ni}(\text{AcAc})_2 \cdot \text{L} \rightarrow \text{Ni}(\text{AcAc})_2 + \text{L}$
 $\text{Ni}(\text{AcAc})_2 \rightarrow \text{pyrolysis}$
- IV. $\text{Ni}(\text{AcAc})_2 \cdot 2\text{L} \rightarrow \text{Ni}(\text{AcAc})_2 \cdot 0.8\text{L} + 1.2\text{L}$
 $\text{Ni}(\text{AcAc})_2 \cdot 0.8\text{L} \rightarrow \text{pyrolysis}$
- V. $\text{Ni}(\text{AcAc})_2 \cdot 2\text{L} \rightarrow \text{Ni}(\text{AcAc})_2 \cdot 0.75\text{L} + 1.25\text{L}$
 $\text{Ni}(\text{AcAc})_2 \cdot 0.75\text{L} \rightarrow \text{pyrolysis}$
- VI. $\text{Ni}(\text{AcAc})_2 \cdot 2\text{L} \rightarrow \text{Ni}(\text{AcAc})_2 \cdot 0.5\text{L} + 1.5\text{L}$
 $\text{Ni}(\text{AcAc})_2 \cdot 0.5\text{L} \rightarrow \text{pyrolysis}$
- VII. $\text{Ni}(\text{AcAc})_2 \cdot \text{L} \rightarrow \text{pyrolysis}$

The adduct of piperazine followed process I. That of morpholine followed process II. The adduct of piperidine followed process III. The adduct of quinoline followed process IV. The adduct of 3-cyanopyridine followed process V. The adducts of pyridine, 3-methylpyridine, 4-methylpyridine and 4-cyanopyridine followed process VI. Finally the adduct of bipyridine followed process VII.

The DSC cures of the adducts are consistent with TG-DTG data. They present several endothermic and exothermic peaks. Endothermic peaks due to the elimination of ligand, elimination of ligand with melting, melting with pyrolysis of the decomposition product or melting with pyrolysis of the adduct are observed. Exothermic peaks due to pyrolysis of the decomposition residues are also observed. Table 3 lists the thermoanalytical data of the adducts.

3.3. Electronic spectra

Table 4 contains the band maxima assignments and calculated ligand field parameters for the adducts. The

ligand field parameters were calculated according to Reedijk et al. [32]. The electronic spectra of the adducts present four absorption bands: The first (ν_1) in the region 10 688–11 145 cm^{-1} , the second (ν_4) in the region 12 641–14 898 cm^{-1} , the third (ν_2) in the region 16 467–17 699 cm^{-1} and the fourth (ν_3) in the region 26 616–29 473 cm^{-1} . According to the number and position of these bands, and considering the magnitude of the crystal field parameters as compared with that of Bolster [33], we conclude that the Ni(II) ion is pseudo-octahedrally surrounded (due to the different kind of atoms, nitrogen and oxygen, present).

3.4. Calorimetric measurements

The standard enthalpies of dissolution of Ni(II) acetylacetonate, ligands and adducts were obtained as previously reported [19]. Because Ni(AcAc)₂ exists as a polymer in the solid state [34], a hypothetical monomer for the calculation of the standard enthalpy of dissolution of Ni(AcAc)_{2(s)} + solvent → Ni(AcAc)_{2(sol)} ($\Delta_1 H^\theta$) was assumed. Table 5 gives the values obtained for the enthalpies of dissolution of Ni(AcAc)₂ ($\Delta_1 H^\theta$), ligand into the solution of Ni(AcAc)₂ ($\Delta_2 H^\theta$) and of the adduct ($\Delta_3 H^\theta$). Uncertainty intervals given in this table are twice the standard deviation of the means of about five replicate measurements on each compound. Combined errors were calculated from the square root of the sum of the squares of the component errors.

From the values obtained for the standard enthalpies of dissolution, and using appropriate thermochemical cycles [19],[35], the following thermochemical parameters were determined: the standard enthalpies of the acid/base reactions ($\Delta_r H^\theta$), the standard enthalpies of formation ($\Delta_f H^\theta$), the standard enthalpies of decomposition ($\Delta_D H^\theta$), the standard lattice 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 $\Delta_r H^\theta_{(g)}$ values can be used to calculate the standard enthalpies of the Ni–N bonds [35]. 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 [19],[35],[42],[43], as melting points and thermal studies showed that the adducts

Table 3
Thermoanalytical data of the compounds Ni(AcAc)₂·nL

Compound	% Mass lost		TG temperature range/K	Species lost	DSC peak temperature/K	Enthalpy/ (kJ mol ⁻¹)
	calculated	observed				
Ni(AcAc) ₂ ·pipz	14.0	13.7	455–491	–0.7pipz	494	46.1
	86.0	84.2	491–719	–Ni(AcAc) ₂ ·1.3pipz ^b	591	178.6
Ni(AcAc) ₂ ·2morph	20.2	2.1 ^a	399–432	–morph	372	42.5
	79.8	19.2	432–746	–Ni(AcAc) ₂ ·morph ^b	451	7.0
Ni(AcAc) ₂ ·2pipd	19.9	77.0	362–395	–pipd	478	72.0
		3.8 ^a		–pipd	563	15.8
		5.4 ^a		–Ni(AcAc) ₂ ^b	463	142.2
		20.2		547	1.2	
		20.6				
Ni(AcAc) ₂ ·2py	28.6	30.0	414–496	–1.5py	441	168.8
	71.4	64.7	496–846	–Ni(AcAc) ₂ ·0.5py ^b	548	2.0
Ni(AcAc) ₂ ·(β-pico) ₂	31.5	6.8 ^a	408–488	–1.5(β-pico)	644	–9.3
		34.9		–Ni(AcAc) ₂ ·0.5(β-pico) ^b	459	165.4
		59.4			565	3.5
		6.2 ^a				
		62.7				
Ni(AcAc) ₂ ·(γ-pico) ₂	31.5	32.0	423–491	–1.5(γ-pico)	361	13.7
	68.5	62.7	491–796	–Ni(AcAc) ₂ ·0.5(γ-pico) ^b	459	122.8
Ni(AcAc) ₂ ·(3-cyanopy) ₂	27.8	5.4 ^a	444–488	–1.25(3-(cyanopy))	558	18.5
		66.0	488–853	–Ni(AcAc) ₂ ·0.75(3-(cyanopy)) ^b	499	155.6
		5.5 ^a			546	13.2
		36.0			638	3.5
Ni(AcAc) ₂ ·(4-cyanopy) ₂	33.6	36.0	442–490	–1.5(4-(cyanopy))	446	47.0
	66.4	57.3	490–853	–Ni(AcAc) ₂ ·0.5(4-(cyanopy)) ^b	510	66.0
Ni(AcAc) ₂ ·bipy	10.0	6.7 ^a	550–866	–Ni(AcAc) ₂ ·bipy ^b	629	3.7
		90.4				513
Ni(AcAc) ₂ ·2quin	30.1	9.6 ^a	474–483	–1.2quin	534	25.9
		68.0		483–806	–Ni(AcAc) ₂ ·0.8quin ^b	578
	69.9	2.5 ^a			485	104.6
					564	11.3
					656	–17.8

^a Residue.

^b Pyrolysis of the compound formed.

Table 4

Band maximum assignments ^a and calculated ligand-field parameters for the compounds Ni(AcAc)₂nL

Compound	ν_1/kk	ν_2/kk	ν_4/kk	ν_3/kk	$D_q \text{ cm}^{-1}$	$B \text{ cm}^{-1}$	D_q/B	β^{+1}
Ni(AcAc) ₂ -pipz	10.69	17.09	28.63	12.83	1069	851	1.26	0.83
Ni(AcAc) ₂ -2.morph	10.89	16.47		14.21	1090	629	1.73	0.61
Ni(AcAc) ₂ -2.pipd	11.15	16.82	28.85	12.76	1115	639	1.74	0.62
Ni(AcAc) ₂ -2.py	11.12	17.53	29.47	12.64	1112	810	1.37	0.79
Ni(AcAc) ₂ -(β -pico) ₂	11.07	17.16			1107	732	1.51	0.71
Ni(AcAc) ₂ -(γ -pico) ₂	10.98	17.06	27.97	14.84	1098	736	1.49	0.72
Ni(AcAc) ₂ -(3-cyanopy) ₂	11.14	17.70	27.76	14.90	1114	851	1.31	0.83
Ni(AcAc) ₂ -(4-cyanopy) ₂	10.81	17.19	26.62	13.44	1082	828	1.31	0.80
Ni(AcAc) ₂ -bipy	10.65	16.82		13.57	1065	785	1.36	0.76
Ni(AcAc) ₂ -2.quin	10.69	16.82	26.94	13.15	1069	771	1.39	0.75

^a $\nu_1=^3T_{2g} \leftarrow ^3A_{2g}$, $\nu_2=^3T_{1g}(\text{F}) \leftarrow ^3A_{2g}$, $\nu_4=^1E_g \leftarrow ^3A_{2g}$, $\nu_3=^3T_{1g}(\text{P}) \leftarrow ^3A_{2g}$, $\beta^+=B/B_0$, $B_0=1030 \text{ cm}^{-1}(\text{Ni}^{2+})$.

Table 5

Enthalpies of dissolution at 298.15 K

Compound	Calorimetric solvent ^a	Number of experiments	$\Delta_r H^\theta / (\text{kJ mol}^{-1})$
Ni(AcAc) ₂	25% HCl 1.2N in methanol	19	(<i>i</i> =1) -3.73 ± 0.13
pipz	1 : 1 Ni(AcAc) ₂ -25% HCl 1.2N in methanol	6	(<i>i</i> =2) -64.89 ± 0.84
Ni(AcAc) ₂ -pipz	25% HCl 1.2N in methanol	4	(<i>i</i> =3) -40.05 ± 0.41
morph	2 : 1 Ni(AcAc) ₂ -25% HCl 1.2N in methanol	6	(<i>i</i> =2) -106.37 ± 1.07
Ni(AcAc) ₂ -2morph	25% HCl 1.2N in methanol	4	(<i>i</i> =3) -22.65 ± 1.16
pipd	2 : 1 Ni(AcAc) ₂ -25% HCl 1.2N in methanol	6	(<i>i</i> =2) 129.93 ± 1.80
Ni(AcAc) ₂ -2pipd	25% HCl 1.2N in methanol	5	(<i>i</i> =3) -62.71 ± 1.38
py	2 : 1 Ni(AcAc) ₂ -25% HCl 1.2N in methanol	6	(<i>i</i> =2) -43.49 ± 0.86
Ni(AcAc) ₂ -2py	25% HCl 1.2N in methanol	5	(<i>i</i> =3) 15.11 ± 0.57
β -pico	2 : 1 Ni(AcAc) ₂ -25% HCl 1.2N in methanol	5	(<i>i</i> =2) -39.22 ± 0.24
Ni(AcAc) ₂ -(β -pico) ₂	25% HCl 1.2N in methanol	4	(<i>i</i> =3) 14.60 ± 1.06
γ -pico	2 : 1 Ni(AcAc) ₂ -25% HCl 1.2N in methanol	5	(<i>i</i> =2) -50.31 ± 1.01
Ni(AcAc) ₂ -(γ -pico) ₂	25% HCl 1.2N in methanol	4	(<i>i</i> =3) 14.91 ± 0.56
3-cyanopy	2 : 1 Ni(AcAc) ₂ -25% HCl 1.2N in methanol	6	(<i>i</i> =2) 37.30 ± 0.55
Ni(AcAc) ₂ -(3-cyanopy) ₂	25% HCl 1.2N in methanol	4	(<i>i</i> =3) 60.04 ± 1.38
4-cyanopy	2 : 1 Ni(AcAc) ₂ -25% HCl 1.2N in methanol	5	(<i>i</i> =2) 30.45 ± 0.23
Ni(AcAc) ₂ -(4-cyanopy) ₂	25% HCl 1.2N in methanol	3	(<i>i</i> =3) 64.88 ± 0.97
bipy	1 : 1 Ni(AcAc) ₂ 25% HCl 1.2N in methanol	3	(<i>i</i> =2) 3.61 ± 0.22
Ni(AcAc) ₂ -bipy	25% HCl 1.2N in methanol	5	(<i>i</i> =3) 7.44 ± 0.40
quin	2 : 1 Ni(AcAc) ₂ -25% HCl 1.2N in methanol	6	(<i>i</i> =2) -33.69 ± 0.33
Ni(AcAc) ₂ -2quin	25% HCl 1.2N in methanol	5	(<i>i</i> =3) 22.08 ± 0.01

^a 25% (v/v) Aqueous HCl 1.2N in methanol.

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: morph>pipd> γ -pico>py>quin> β -pico>4-cyanopy>3-cyanopy and pipz>bipy. Using the $\bar{D}_{(\text{Ag-N})}$ values, we obtain the sequence morph>4-cyanopy>quin>3-cyanopy> γ -pico>pipd> β -pico>py and pipz>bipy. The

expected order for pyridine and derivatives would be γ -pico> β -pico>py>3.cyanopy>4-cyanopy, due to an inductive effect of substitution of one hydrogen atom in the pyridine ring by the electronic donor methyl group in β - or γ -pico or by electronic withdrawing cyano group in 3- or 4-cyanopy. This causes the increase or the decrease of the electronic density available for bonding on the nitrogen atom of the ring

Table 6
Summary of the thermochemical results (kJ mol⁻¹)

Compound	$\Delta_r H^\theta$	$\Delta_f H^\theta$	$\Delta_s H^\theta$ or $\Delta_1 H^\theta$	$\Delta_M H^\theta$	$\Delta_D H^\theta$	$\Delta_r H^\theta(\text{g})$	$\bar{D}_{(\text{Ni}-\text{N})}$
Ni(AcAc) _{2(s)}		-910.6±2.1 ^a	95.4				
pipz _(s)		-45.6±1.6 ^b	84.2 ^c				
morph ₍₁₎		-170.2 ^c	42.3 ^c				
pipd ₍₁₎		-88.0±1.0 ^b	39.1±1.8 ^b				
py ₍₁₎		101.2±0.7 ^b	40.2 ^b				
β-pico ₍₁₎		61.9±0.5 ^b	44.4±0. ^b				
γ-pico ₍₁₎		58.5±1.1 ^b	45.3±0.4 ^b				
3-cyanopy _(s)		84.0±2.1 ^d	43.0±1.4 ^d				
4-cyanopy _(s)		77.8±2.3 ^d	46.7±1.5 ^d				
bipy _(s)		216.4±7.4 ^c	81.93±0.33 ^f				
quin ₍₁₎		166.1±1.9 ^d	59.7±1.0 ^d				
Ni(AcAc) ₂ -pipz _(s)	-28.57±0.94	-984.8±2.8		-208.2±1.7	112.8±1.4	-124.0±1.4	62.0±0.7
Ni(AcAc) ₂ -2morph _(s)	-87.81±1.58	-1338.8±3.3		-267.8±2.7	172.4±2.5	-225.5±2.9	112.8±1.5
Ni(AcAc) ₂ -2pipd _(s)	-70.95±2.27	-1157±3.7		-244.6±4.4	149.2±4.3	205.5±4.7	102.8±2.4
Ni(AcAc) ₂ -2py _(s)	-62.33±1.04	-770.5±2.7		-238.1±1.4	142.7±1.0	187.9±1.4	94.0±0.7
Ni(AcAc) ₂ -(β-pico) _{2(s)}	-57.55±1.09	-844.4±2.6		-241.8±1.5	146.4±1.1	197.4±1.5	98.7±0.8
Ni(AcAc) ₂ -(γ-pico) _{2(s)}	-68.95±1.16	-862±3.3		-255.0±1.7	159.6±1.4	-209.7±1.8	104.9±0.9
Ni(AcAc) ₂ -(3-cyanopy) _{2(s)}	-26.47±1.49	-861.1±8.1		-299.8±5.9	204.39±5.83	-210.8±6.6	105.4±3.3
Ni(AcAc) ₂ -(4-cyanopy) _{2(s)}	-38.61±1.01	-867.0±8.1		-300.8±7.1	205.4±7.1	217.2±8.0	108.6±4.0
Ni(AcAc) ₂ -bipy _(s)	-7.56±0.47	-701±7.7		-108.9±1.2	89.49±0.57	-103.0±1.2	51.5±0.6
Ni(AcAc) ₂ -2quin _(s)	-59.50±0.35	-737.9±4.4		274.3±2.3	178.9±1.1	-214.6±2.5	107.3±1.3

^a Ref. [36].

^b Ref. [37].

^c Ref. [38].

^d Ref. [39].

^e Ref. [40].

^f Ref. [41].

relative to pyridine. The effect is stronger in *p*-substitution than in *m*-substitution. The order observed presents inversion between 3- and 4-cyanopy and both of them are more basic than py and other pyridine derivatives, if we use the basicity order obtained from $\bar{D}_{(\text{Ni}-\text{N})}$ values. Otherwise, it is the expected order. The basicity order observed could be due to the contribution of another kind of interaction like hydrogen bonding between nitrogen atom from cyano groups and carbon atoms from acetylacetonate ions [39], this effect being stronger in 4- than in 3-cyanopy. Comparing pyridine with quinoline, the latter is expected to be more basic than the former due to the conjugation of two aromatic rings that increase the electronic density available over the nitrogen atom. This is also observed. The expected basicity order for saturated heterocycle amines would be pipd>pipz>morph due to an inductive effect of substitution of one carbon atom in the ring of pipd by the more electronegative atoms of nitrogen (in pipz) or oxygen (in morph), that leads

to the decrease of the electronic density available for bonding on the nitrogen atom of the ring. We observed morph>pipd. The inversion of the expected order could be the contribution to another kind of interaction, such as hydrogen bonding between carbon atoms from acetylacetonate ions and oxygen atoms from morpholine ligands. The adduct of pipz has another stoichiometry and cannot be compared with morph and pipd adducts. Comparing the ligand field parameter D_q with the thermochemical parameter $\bar{D}_{(\text{Ni}-\text{N})}$ for the adducts of the same stoichiometry, we observed for the adducts of py, β-pico, pipd and 3-cyanopy that the D_q values increase with the increase of $\bar{D}_{(\text{Ni}-\text{N})}$ values, indicating that the splitting of orbitals of Ni(II) ion is favoured by stronger Ni–N bonds (Fig. 1), as it was also observed for the Co(II) adducts with the same ligands [39]. Comparing β^+ values with $\bar{D}_{(\text{Ni}-\text{N})}$ values, we observed for adducts of 3-cyanopy, 4-cyanopy, quin, γ-pico and morph that the β^+ values decrease with the increase of the $\bar{D}_{(\text{Ni}-\text{N})}$ values, indicating that

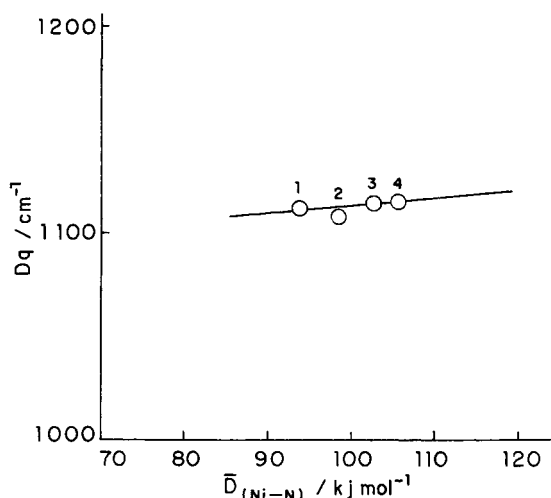


Fig. 1. Correlation of Dq values with $\bar{D}_{(Ni-N)}$ values for the adducts of $Ni(AcAc)_2$ with (1) py, (2) β -pico, (3) pipd, and (4) 3-cyanopy.

the covalence of the d -orbitals of the $Ni(II)$ ion is higher as the $Ni-N$ bond is stronger (Fig. 2).

In conclusion $Ni-N$ bonds in the adducts of $Ni(II)$ acetylacetonate are stronger than the $Co-N$ bonds in adducts of $Co(II)$ acetylacetonate formed with the same heterocyclic bases.

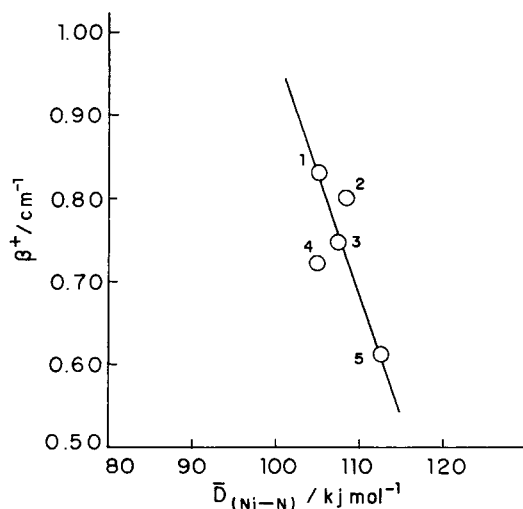


Fig. 2. Correlation of β^+ values with $\bar{D}_{(Ni-N)}$ values for the adducts of $Ni(AcAc)_2$ with (1) 3-cyanopy, (2) 4-cyanopy, (3) quin, (4) γ -pico and (5) morph.

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