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

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Abstract

The compounds $Co(AcAc)_2.nL$, where AcAc represents acetylacetonate, L the 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); $n = 1$ or 2) were synthesized and characterized by melting points, elemental analysis, thermal studies and electronic and IR spectroscopy. The enthalpies of dissolution in 10% (v/v) ethanolamine in methanol, 10% (v/v) triethanolamine in azeotropic methanol–dichlorethane mixture, 10% (v/v) diethanolamine in azeotropic methanol–dichlorethane mixture or 25% (v/v) aqueous HCl 1,2 N in methanol were measured. Appropriate thermochemical cycles then give the standard enthalpy change 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 standard lattice enthalpies ($\Delta_M H^\theta$) and the standard enthalpies of the Lewis acid/base reactions in the gaseous phase ($\Delta_f H^\theta(g)$). The mean standard enthalpies of the cobalt-nitrogen bonds have been estimated. © 1997 Elsevier Science B.V.

Keywords: Cobalt(II); Co(II) acetylacetonate; Co–N bonds; Thermochemical parameters; Thermochemistry

1. Introduction

The synthesis of complexes of divalent 3*d*-electron elements with β-diketone chelates and several heterocyclic bases is found in the literature [1–11]. However, no information about the enthalpies of the transition element–nitrogen bonds in these kind of compounds is available. Adducts of Co(II) acetylacetonate chelate with heterocyclic bases were synthesized with the purpose of obtaining the enthalpies involved in the formation of the adducts and to establish correlations between the bond energies and other thermochemical parameters. The ligand field parameters of the adducts were also calculated in order to find possible correlations between them and the thermochemical parameters. The effect of the substitution of one hydrogen atom of the pyridine ring by the electron donator group methyl or the electronic withdrawing group cyano on the cobalt(II)–nitrogen bond energy was also studied.

2. Experimental

2.1. Chemicals

Co(II) acetylacetonate was prepared by the Ellern et al. method [12]. The compound was recrystallized

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from methanol and dehydrated under reduced pressure at 363 K. The chelate was pink and the results of the elemental analysis gave: Co – 22.86; C – 46.39; and H – 5.37 mass per cent (theoretical: Co – 22.92; C – 46.70; and H – 5.49). Piperazine (99% Aldrich) was purified by recrystalization from methanol (mp 107–108°C). Morpholine (99% A.C.S. Aldrich) pyridine (ACS Reagent), 3-methylpyridine (Baker), quinoline (98% Aldrich) and piperidine (99% RPE, Analyticals, Carlo Erba), were purified by distillation using an efficient column and stored over 4 Å molecular sieves (b.p. 123–124, 111–112, 139–140, 140–141, 111–112/20 mmHg and 103–104°C, respectively). Further, 2,2′-Bipyridine (99% Aldrich) was purified by recrystallization from ethanol according to the method described by Gallagher et al. [13] (m.p. 193–194°C). 3-cyanopyridine (98% Aldrich) and 4-cyanopyridine (98% Aldrich) were purified by recrystallization from methanol (m.p. 49–50° and 77–78°C, respectively). Other solvents used in the synthesis of the adducts were purified by distillation and stored over the Linde 4 Å molecular sieves.

2.2. *Analytical*

Carbon, hydrogen and nitrogen were determined by microanalytical procedures. The cobalt content was determined by complexometric titration with 0.01 M EDTA solution [14] of the aqueous solution of adduct samples. The capillary melting points of the adducts were determined using a UNIMELT equipment from Thomas Hover.

2.3. *Adduct synthesis*

The adducts were prepared by the reaction of Co(II) acetylacetonate and ligands in solution. A typical procedure is given below.

2.3.1.

To a solution of 1.2 g of Co(AcAc)$_2$ (4.7 mmol) in 50 ml of hot methanol, 0.809 of piperazine (9.4 mmol) in 10 ml of methanol was added slowly and dropwise with stirring. The mixture was cooled in an ice bath and the solid formed was filtered and washed with three portions of 10 ml of petroleum ether. The product was dried for several hours in vacuo and stored in a desiccator over calcium chloride. In nearly all the cases, petroleum ether was used as a solvent for washing. In the case of the adduct of piperidine, the Co(II) was dissolved in 10 ml of hot piperidine. The solution was concentrated by heating and, thereafter, cooled in an ice bath. After filtration, the solid obtained was dried for several hours in vacuo.

2.4. *IR 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 made 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) ranges. TG calibration for weight was made using calcium oxalate as a standard. TG calibration for temperature was made using metallic aluminium as a standard mp (660.37°C). DSC calibration was made using metallic indium as a standard (m.p. 156.73°C, $\Delta_s{}^{\ell}H^{\theta} = 28.4\ \mathrm{J\ g^{-1}}$).

2.6. *Calorimetric measurements*

All the sodium calorimetric determinations were carried out in an LKB 8700-1 precision calorimeter as described elsewhere [15]. The solution calorimeter measurements were performed by dissolving samples of 13–100 mg of the adduct or Co(II) acetylacetonate in 100 ml of the appropriate solvent and the ligand in this last solution maintaining a molar relation equal to the stoichiometry of the adduct. The accuracy of the calorimeter was carried out by determining the heat of dissolution of tris [(hydroxymethyl) amino] methane in 0.1 mol dm^{-3} HCL. The result (-29.78 ± 0.03 kJ mol^{-1}) is in agreement with the value recommended by IUPAC [16] (-29.763 ± 0.003 kJ mol^{-1}).

2.7. Electronic spectra

Spectra in the 350–2000 nm region were obtained with a UV-VIS-NIR Varian-Cary 2300 spectrophotometer for the acetonitrile solutions of the adducts (5 mM). A UV-VIS-NIR Varian-Carry 5G spectrophotometer with a standard reflectance attachment was used to obtain spectra for the solid adducts.

3. Results and discussion

All the adducts obtained were solids. The yields range from 39 to 87%. 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 $\nu_{(C-O)}$ and $\nu_{(C-C)}$ in the 1600–1500 cm^{-1} region are based on the works of Pinchas et al. [17] and Bennke and Nakamoto [18]. Two bands are observed in the 1600–1500 cm^{-1} region for the adducts. These bands are assigned to C–O (1599–1580 cm^{-1}) and C–C (1529–1512 cm^{-1}) stretching vibrations. The shifts to lower frequencies observed in the 570–405 cm^{-1} region of $\nu_{(C-O)}$, $\nu_{(C-C)}$ [19] and $\nu_{(Co-O)}$ [9] found in the adducts, are much more marked than those of the Co(II) acetylacetonate chelate [9], indicating that the amines are bonded to the cobalt ion. Considerable shifts to lower frequencies of the $\nu_{(N-H)}$ bands of ligands after coordination is also indicative of coordination. These shifts show that piperazine, morpholine and piperidine are coordinated to the cobalt ion by means of the nitrogen atom of their N–H group [20,21]. In the morpholine adduct, the positive shift of C–O–C stretching vibration with respect to free morpholine excludes the possibility of oxygen-to-cobalt coordination [21]. The change observed in the H–N–C deformation region (869–815 cm^{-1}) also affords evidence of the coordination of the nitrogen atom of the ligands [22]. The bands observed in the 600–400 cm^{-1} region are assigned to Co–O modes [7,23]. They are shifted to lower frequencies by adduct formation. The coordinated pyridine is distinguished from free pyridine by the presence in the adduct of a weak band at 1218 cm^{-1} and by the dislocation of bands found at 1573, 584 and 431 cm^{-1} in the free pyridine [24] to higher frequencies. The weak band was observed, but two of the three bands were overlapped by vibrations of the Co(II) chelate in the same region. The infrared spectra of β-Pico and γ-Pico adducts show appreciable dislocations towards higher frequencies of the bands at 1585, 1545 and 1206 cm^{-1} in the free ligands [25,26]. Only the dislocation of the third band is observed as the first two bands are covered by Co(II) acetylacetonate bands. For 3- and 4-cyanopyridine adducts this last band is observed at 1257 cm^{-1} (1219–1216 cm^{-1} in free ligands). The infrared data can be interpreted in terms of coordination of these ligands through the heterocyclic nitrogen atom to the cobalt ion [24–26]. The infrared spectra of the Bipy

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

Compound	Yield	m.p. [a]/K	Appearance [b]	C		H		N		Cobalt	
				Calc	Found	calc	found	calc	found	calc	found
Co(AcAc)$_2$.Pipz	87	533–535	ro, cr	48.98	49.23	7.05	6.94	8.16	8.27	17.17	17.30
Co(AcAc)$_2$.2Morph	50	442–451	s, re, cr	50.12	49.98	7.48	7.24	6.49	6.26	13.66	13.66
Co(AcAc)$_2$.2Pipd	60	419–421	sa, re, cr	56.20	55.92	8.49	8.38	6.55	6.29	13.79	13.58
Co(AcAc)$_2$.2Py	52	422–423	re, cr	57.84	57.49	5.82	5.68	6.74	6.63	14.19	13.96
Co(AcAc)$_2$.2β-Pico	72	427	s, or, cr	59.59	60.00	6.36	6.10	6.32	6.40	13.29	13.00
Co(AcAc)$_2$.2γ-Pico	72	453–456	or, cr	59.59	59.73	6.36	6.06	6.32	6.30	13.29	13.01
Co(AcAc)$_2$.(3-cyanopy)$_2$	87	461–462	s, or, cr	56.78	57.06	4.77	4.53	12.04	12.09	12.66	12.41
Co(AcAc)$_2$.(4-cyanopy)$_2$	87	490–491	s, or, cr	56.78	57.08	4.77	4.55	12.04	12.11	12.66	12.70
Co(AcAc)$_2$.Bipy	62	488–490	s, or, cr	58.12	57.87	5.36	5.05	6.78	6.52	14.26	14.39
Co(AcAc)$_2$.2Quin	79	460–461	or, cr	62.24	62.48	5.48	5.35	5.43	5.47	11.43	11.25

[a] Melting with decomposition.

[b] Key: ro – rose; re – red; or – orange; sa – salmon; s – slight; and cr – crystals.

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

Compound	$\nu_{(C-O)}$	$\nu_{(C-C)}$	$\nu_{(Co-C)}$	Ligands bands								
				$\nu_{(N-H)}$	$\nu_{(C-C)}$	$N_{(C\equiv N)}$	ring	$\nu_{(C-O-O)}$	$\delta_{(H-N-C)}$	$\alpha_{(C-C-C)}$	$\phi_{(C-C)}$	New band
$Co(AcAc)_2$	1595vs	1529vs	570s									
Pipz				3328m					861m, 815s			
$Co(AcAc)_2$.Pipz	1586vs	1513vs	553s	3258m					869s			
Morph				3320m	1452s			1097s	889m, 835s			
$Co(AcAc)_2$.2Morph	1593vs	1513vs	551s, 411s	3278m				1107s	874s, 767s			
Pipd				3276m	1467s				860, 825m			
$Co(AcAc)_2$.2Pipd	1599vs	1515vs	560s	3221m					869s			
Py					1573sh					584s	431m	
$Co(AcAc)_2$.2Py	1574vs	1512vs	557s		n.o.					624s	n.o.	1218w
β-Pico					1572sh		1206m					
$Co(AcAc)_2$.2β-Pico			556s, 410s		n.o.		1242w					
γ-Pico					1585s, 1545s		1206s					
$Co(AcAc)_2$.2γ-Pico	1593vs	1514vs	552s, 494s		n.o.		1228s					
3-cyanopy						2231s	1219s					
$Co(AcAc)_2$.(3-cyanopy)$_2$	1589vs	1515vs	555m, 416s			2234s	1257m					
4-cyanopy						2236s	1216s					
$Co(AcAc)_2$.(4-cyanopy)$_2$	1546s	1513vs	563s, 412s			2236s	1257s					
Bipy												
$Co(AcAc)_2$.Bipy	1589vs	1514vs	551m, 405m									1290m, 790w
Quin												
$Co(AcAc)_2$.2Quin	1580vs	1512vs	552w, 492m									1260s

[a] Key: α – ring deformation in plane; ϕ – ring deformation out of plane; ν – stretching; δ – angular deformation; ring – ring breathing; and n.o. – not observed. Intensity of bands: vs – very strong; s – strong; m – medium; w – weak; and sh – shoulder.

adduct show the appearance of new bands after coordination. Two new bands appear at 1290 and 790 cm^{-1}, both of which are absent in free Bipy and are due to adduct formation [27]. The infrared spectra of the Quin adduct show dislocation of several bands with respect to the free ligand [6]. A new band is observed at 1260 cm^{-1} after 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 cobalt ion [6,27]. Table 2 shows the extracted IR spectral data of the adducts.

3.2. *Thermal studies*

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

I. $Co(AcAc)_2.2L \rightarrow Co(AcAc)_2.L + L$
$Co(AcAc)_2.L \rightarrow$ pyrolysis
II. $Co(AcAc)_2.2L \rightarrow Co(AcAc)_2.0.5L + 1.5L$
$Co(AcAc)_2.0.5L \rightarrow$ pyrolysis
III. $Co(AcAc)_2.2L \rightarrow$ pyrolysis
IV. $Co(AcAc)_2.L \rightarrow Co(AcAc)_2.0.5L + 0.5L$
$Co(AcAc)_2.0.5L \rightarrow$ pyrolysis
V. $Co(AcAc)_2.L \rightarrow$ pyrolysis

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

The DSC curves of the adducts are consistent with the TG-DTG data. They present several endothermic and exothermic peaks. For the piperazine adduct, two exothermic peaks at 493 and 510 K – due to the decomposition of the adduct – are observed, followed by an endothermic peak at 528 K due to melting and decomposition of $Co(AcAc)_2.0.5$ Pipz. As for the other adducts, several endothermic peaks due to elimination of ligand, elimination of ligand with melting, melting with pyrolysis of the decomposition residue and melting with decomposition of the adduct or pyrolysis of the adduct are observed. Exothermic peaks due to the decomposition of the adduct or the pyrolysis of the decomposition residues also are observed. Table 3 lists the thermoanalytical data.

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. [28]. The electronic spectra of the adducts present three adsorption bands: the first (ν_1) in the 9120–10560 cm^{-1}, the second (ν_2) in the 12740–16350 m^{-1} and the third (ν_3) in the 18280–19560 cm^{-1} regions. According to the number and position of these bands and considering the magnitude of the crystal field parameters as compared with that of Bolster [29], we conclude that the Co(II) ion is octahedrally surrounded (or more strictly, pseudo-octahedrally due to the different kind of atoms – nitrogen and oxygen – present).

3.4. *Calorimetric measurements*

The standard enthalpies of dissolution of Co(II) acetylacetonate, ligands and complexes ($\Delta_i H^\theta$) were obtained as previously reported [15]. Because $Co(AcAc)_2$ exists as a polymer in the solid state [30], a hypothetical monomer for the calculations of the standard enthalpy of dissolution of $Co(AcAc)_{2(s)}$ + sol. $\rightarrow Co(AcAc)_{2(sol)} \Delta_1 H^\theta$ was assumed. Table 5 gives the values obtained for the enthalpies of dissolution of $Co(AcAc)_2$ ($\Delta_1 H^\theta$) and ligand into the solution of $Co(AcAc)_2$ ($\Delta_2 H^\theta$) and of the adduct ($\Delta_3 H^\theta$). 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 dissolution and using appropriate thermochemical cycles [15,31], 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 Co–N bonds [31]. Table 6

Table 3
Thermoanalytical data of the compounds $Co(AcAc)_2.nL$

Compound	% Mass lost		TG temperature range/K	Species lost	DSC peak temperature/K	Enthalpy/(kJ mol^{-1})
	calc	obs.				
$Co(AcAc)_2$.Pipz	17.2	14.7	418–445	–0.5.Pipz	493	−1.3
	82.8	84.0	445–553	–$Co(AcAc)_2$.0.5.Pipz [b]	510	−12.0
		0.2 [a]			528	43.7
$Co(AcAc)_2$.2.Morph	20.2	18.7	326–415	–Morph	358	5.6
	79.8	79.6	415–753	–$Co(AcAc)_2$.Morph [b]	443	63.1
		3.2 [a]			548	24.8
$Co(AcAc)_2$.2Pipd	20.2	17.0	349–375	–Pipd	428	51.0
	79.8	73.8	375–482	–$Co(AcAc)_2$.Pipd [b]	554	28.1
		5.9	482–778			
		2.5 [a]				
$Co(AcAc)_2$.2Py	100	94.7	429–486	–$Co(AcAc)_2$.2Py	426	42.4
		3.3	697–733		718	−184.9
		4.0 [a]				
$Co(AcAc)_2$.2β-Pico	31.5	29.9	368–403	−1.5β-Pico	429	50.6
	68.5	65.9	403–488	–$Co(AcAc)_2$.0.5β-Pico [b]	513	11.1
		4.26	660–686		553	22.6
$Co(AcAc)_2$.2γ-Pico	21.0	22.7	386–412	–γ-Pico	459	64.3
	79.0	74.0	412–486	–$Co(AcAc)_2$.γ-Pico [b]	513	1.4
		3.2 [a]	486–753		538	−11.5
$Co(AcAc)_2$.(3-cyanopy)$_2$	100	93.9	419–733	–$Co(AcAc)_2$(3-cyanopy)$_2$ [b]	469	86.2
		6.1 [a]			503	−12.0
					531	−11.7
$Co(AcAc)_2$.(4-cyanopy)$_2$	100	90.6	442–633	–$Co(AcAc)_2$.(4-cyanopy)$_2$ [b]	416	24.8
		3.3	757–800		494	60.7
		6.1 [a]			513	−13.3
					545	−4.2
$Co(AcAc)_2$.Bipy	100	94.6	494–539	–$Co(AcAc)_2$.Bipy [b]	372	12.5
		5.0 [a]			511	64.4
$Co(AcAc)_2$Quin	100	99.1	436–523	–$Co(AcAc)_2$.2Quin [b]	463	83.9
		0.7[a]			512	47.3

[a] Residue.

[b] Pyrolyses of the compound formed.

Table 4
Band maxima assignments [a] and calculated ligand-field parameters for the compounds $Co(AcAc)_2.nL$

Compound	ν_1 kK	ν_2 kK	ν_3 kK	Charge transfered band	D_q cm^{-1}	B cm^{-1}	D_q/B	β^+
$Co(AcAc)_2$.Pipz	9.70	12.74	18.28	26.68	1051	638	1.65	0.66
$Co(AcAc)_2$.Morph	9.12	—	18.28	25.16	993	679	1.46	0.70
$Co(AcAc)_2$.2Pipd	9.29	—	18.84	25.79	1012	707	1.43	0.73
$Co(AcAc)_2$.2Py	9.92	16.35	19.33	28.72	1078	699	1.54	0.72
$Co(AcAc)_2$.2β-Pico	10.04	15.41	18.73	25.16	1087	645	1.69	0.66
$Co(AcAc)_2$.2γ-Pipo	10.14	16.12	18.61	25.57	1096	630	1.74	0.65
$Co(AcAc)_2$.(3-cyanopy)$_2$	10.56	15.59	19.56	24.17	1142	669	1.71	0.69
$Co(AcAc)_2$.(4-cyanopy)$_2$	9.70	15.93	18.73	25.16	1053	670	1.57	0.69
$Co(AcAc)_2$.Bipy	9.55	—	18.74	29.96	1038	682	1.52	0.70
$Co(AcAc)_2$.2Quin	9.61	15.83	18.52	25.40	1043	661	1.58	0.68

[a] $\nu_1 = {}^4T_{2\,g} \leftarrow {}^4T_{1\,g}(F)$; $\nu_2 = {}^4A_{2\,g} \leftarrow {}^4T_{1\,g}(F)$; $\nu_3 = {}^2P, {}^2G, {}^4T_{1\,g}(P) \leftarrow {}^4T_{1\,g}(F)$.
$\beta^+ = B/B_0$; $B_0 = 971\ cm^{-1}$ (Co^{2+}).

lists the values obtained for all these thermochemical parameters for the adducts. For the determination of $\Delta_rH^\theta(g)$, 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 [15,31,37,38], 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 either.

Table 5
Enthalpies of dissolution at 298.15 K

Compound	Calorimetric solvent [a]	No. of experiment	Δ_iH^θ/(kJ mol^{-1})
$Co(AcAc)_2$	10% EA in methanol	5	($i = 1$) -100.27 ± 2.47
Pipz	1 : 1 $Co(AcAc)_2$-10% EA in methanol	4	($i = 2$) -7.12 ± 0.31
$Co(AcAc)_2$.Pipz	10% EA in methanol	5	($i = 3$) -88.70 ± 2.73
$Co(AcAc)_2$	10% TEA in Azeo DiClE-methanol	3	($i = 3$) -16.13 ± 0.18
Morph (I)	2 : 1 $Co(AcAc)_2$-10% TEA in Azeo.DiClE-methanol	4	($i = 2$) -17.52 ± 0.12
$Co(AcAc)_2$.2Morph	10% TEA in Azeo.DiClE-methanol	3	($i = 3$) 52 ± 0.77
$Co(AcAc)_2$	10% DEA in Azeo.DiClE-methanol	4	($i = 1$) -7.48 ± 0.72
Pipd	2 : 1 $Co(AcAc)_2$-10% DEA in Azeo.DiClE-methanol	5	($i = 2$) -27.69 ± 1.47
$Co(AcAc)_2$.2Pipd	10% DEA in Azeo.DiClE-Methanol	6	($i = 3$) 25.37 ± 0.36
$Co(AcAc)_2$	25% HCl 1.2 N in methanol	20	($i = 1$) -20.61 ± 0.18
Py	2 : 1 $Co(AcAc)_2$-25% HCl 1.2 N in methanol	4	($i = 2$) -44.73 ± 0.34
$Co(AcAc)_2$2Py	25% HCl 1.2 N in methanol	4	($i = 3$) -0.70 ± 0.09
β-Pico	2 : 1 $Co(AcAc)_2$-25% HCl 1.2 N in methanol	4	($i = 2$) -44.64 ± 1.26
$Co(AcAc)_2$.2β-Pico	25% HCl 1.2 N in methanol	5	($i = 3$) 0.84 ± 0.05
γ-Pico	2 : 1 $Co(AcAc)_2$-25% HCl 1.2 N in methanol	4	($i = 2$) -53.13 ± 0.78
$Co(AcAc)_2$.2γ-Pico	25% HCl 1.2 N in methanol	3	($i = 3$) -1.83 ± 0.11
3-cyanopy	2 : 1 $Co(AcAc)_2$-25% HCl 1.2 N in methanol	3	($i = 2$) 48.60 ± 0.29
$Co(AcAc)_2$(3-cyanopy)$_2$	25% HCl 1.2 N in methanol	3	($i = 3$) 48.60 ± 0.29
4-cyanopy	2 : 1 $Co(AcAc)_2$-25% HCl 1.2 N in methanol	6	($i = 2$) 28.78 ± 0.67
$Co(AcAc)_2$.(4-cyanopy)$_2$	25% HCl 1.2 N in methanol	4	($i = 3$) 48.46 ± 0.92
Bipy	1 : 1 $CO(AcAc)_2$-25% HCl 1.2 N in methanol	4	($i = 2$) -3.18 ± 0.18
$Co(acAc)_2$.Bipy	25% HCl 1.2 N in methanol	4	($i = 3$) 11.88 ± 0.56
Quin	2 : 1 $Co(AcAc)_2$-25% HCl 1.2 N in methanol	4	($i = 2$) -33.73 ± 0.33
$Co(AcAc)_2$.2Quin	25% HCl 1.2 N in methanol	5	($i = 3$) 18.18 ± 0.45

[a] 25% (v/v) aqueous HCl 1.2 N in methanol; 10% (v/v) ethanolamine in methanol; 10% (v/v) triethanolamine in azeotropic diclorethane-methanol 10% Diethanolamine in azetropic diclorethane-methanol.

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

Compound	$\Delta_r H^\theta$	$\Delta_f H^\theta$	$\Delta_s{}^g H^\theta$ or $\Delta_\ell{}^g H^\theta$	$\Delta_M H^\theta$	$\Delta_D H^\theta$	$\Delta_r H^\theta(g)$	$\bar{D}$ (Co–N)
$Co(AcAc)_{2(s)}$		-884.1 ± 2.1 [a]	81.2 ± 1.0 [a]				
$Pipz_{(s)}$		-45.6 ± 1.6 [b]	84.2 [c]				
$Morph_{(\ell)}$		−170.2 [c]	42.3 [c]				
$Pipd_{(\ell)}$		-88.0 ± 1.0 [b]	39.1 ± 1.8 [b]				
$Py_{(\ell)}$		101.2 ± 0.7 [b]	40.2 [b]				
β.$Pico_{(\ell)}$		61.9 ± 0.5 [b]	44.4 ± 0.0 [b]				
γ-$Pico_{(\ell)}$		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 [e]	81.93 ± 0.33 [b]				
$Quin_{(\ell)}$		116.1 ± 1.9 [g]	59.7 ± 1.0 [g]				
$Co(AcAc)_2.Pipz_{(s)}$	-18.69 ± 3.69	-948.4 ± 4.5		-184.1 ± 4.0	108.9 ± 3.8	-99.9 ± 4.1	50.0 ± 2.3
$Co(AcAc)_2.2Morph_{(s)}$	-86.31 ± 0.80	-1310.8 ± 2.5		-252.1 ± 1.6	170.9 ± 2.2	-209.8 ± 2.6	104.9 ± 1.3
$Co(AcAc)_2.2Pipd_{(s)}$	-60.54 ± 1.68	-1120.6 ± 3.4		-219.9 ± 4.1	138.7 ± 2.5	-180.8 ± 4.5	90.4 ± 2.3
$Co(AcAc)_2.2Py_{(s)}$	-64.64 ± 0.40	-884.1 ± 2.1		-226.2 ± 1.1	145.0 ± 0.4	-186.0 ± 1.1	93.0 ± 0.6
$Co(AcAc)_2.2\beta$-$Pico_{(s)}$	-66.09 ± 1.27	-826.4 ± 2.7		-236.1 ± 1.6	154.9 ± 0.4	-191.7 ± 1.6	95.9 ± 0.8
$Co(AcAc)_2.2\gamma$-$Pico_{(s)}$	-71.91 ± 0.81	-839.0 ± 2.5		-243.7 ± 1.5	162.5 ± 0.9	-198.4 ± 1.6	99.2 ± 0.8
$Co(AcAc)_2.2(3$-$cyanopy)_{2(s)}$	-33.68 ± 0.63	-841.8 ± 7.9		-292.8 ± 3.1	119.7 ± 1.5	-203.8 ± 6.4	101.9 ± 3.2
$Co(AcAc)_2.2(4$-$cyanopy)_{2(s)}$	-40.29 ± 1.14	-842.6 ± 8.2		-288.7 ± 3.8	133.7 ± 2.1	-205.1 ± 8.0	102.6 ± 4.0
$Co(AcAc)2.Bipy_{(s)}$	-11.91 ± 0.62	-679.6 ± 7.7		-175.0 ± 1.2	938.4 ± 0.70	-93.1 ± 1.3	46.6 ± 0.7
$Co(AcAc)_2.2Quin_{(s)}$	-72.52 ± 0.59	-724.4 ± 4.4		-273.1 ± 2.3	191.9 ± 1.2	-213.4 ± 2.5	106.7 ± 1.3

[a] Ref. [32].
[b] Ref. [33].
[c] Ref. [34].
[d] See text.
[e] Ref. [35].
[f] Ref. [36].
[g] See text.

For the calculation of the standard enthalpy of formation and other thermochemical parameters of the adducts, it was necessary to calculate the standard enthalpies of formation and sublimation or vaporization of the ligands 3-, 4-cyanopy and Quin, as their values are not found in the literature. We calculated them by a group contribution method [39–41], from enthalpy values for β-, γ-Pico and Py, respectively. Based on the $\Delta_r H^\theta$ values for the adducts of the same stoichiometry we obtain the basicity sequence: Morph > Quin > γ-Pico > β-Pico > Py > Pipd > 4-cyanopy > 3-cyanopy and Pipz > Bipy. The same sequence is obtained by using the $\bar{D}$ (Co–N) values except for the inversion between Morph and Quin and 4-cyanopy > 3-cyanopy appearing after Morph. The expected order would be γ-Pico > β-Pico > Py > 3-cyanopy > 4-cyanopy for pyridine and derivatives, due to an inductive effect of substitution of one hydrogen atom in the pyridine ring by the electronic donator methyl group in β- or γ-Pico; or by the electronic withdrawing cyano group in cyanopy. The electronic density in the aromatic ring is increased in the first case and decreased in the second. It is then expected that the electronic density available for bonding in the nitrogen atom is higher for β- or γ-Pico than in Py; and lower in cyanopy than in Py. The inductive effect is stronger in *p*-substitution than in *m*-substitution. The order observed presents inversion between 3- and 4-cyanopy. Otherwise, it is the expected order obtained from the $\Delta_r H^\theta$ values. The inversion could be due to the contribution of another kind of interaction as hydrogen bonding between nitrogen atoms (from cyano groups) and carbon atoms (from acetylacetonate ions) in the adduct $(Co(AcAc)_2$.$(4$-$cyanopy)_2$ and/or a steric hindrance of *m*-cyano group in the adduct $Co(AcAc)_2$.$(3$-$cyanopy)_2$, leading to the inversion of the expected order of basicity between 4- and 3-cyanopy. Comparing quinoline with

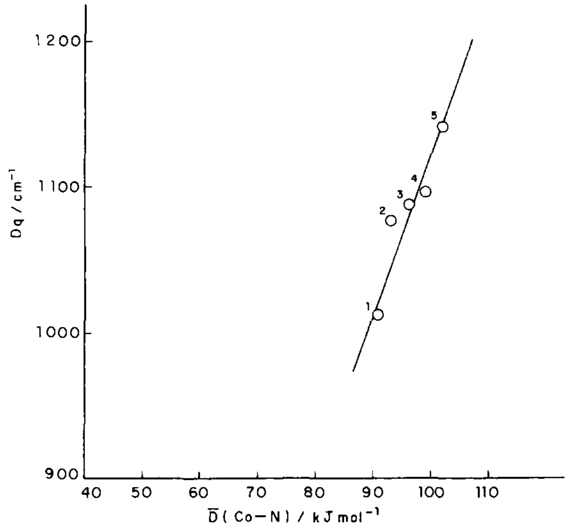

Fig. 1. Correction of D_q with $\bar{D}_{(Co–N)}$ values for the adducts of Co(AcAc)$_2$ with: (1) – Pipd, (2) – Py, (3) – β-pico, (4) γ-pico and (5) 3-cyanopy.

pyridine, the former is expected to be more basic than the latter due to the conjugation of two aromatic rings that increase the electronic density available over the nitrogen atom; this is also observed. Comparing piperidine with pyridine, the former would be less basic than the latter due to the loss of the aromatic character by saturation of double bonds, leading to the decrease of the electronic density available on the nitrogen atom; this too is observed. Between piperazine and bipyridine, the latter would be expected to be more basic due to the disposal of electronic density from the aromatic rings. It is observed that piperazine is better base to Co(II) ion than bipyridine. The more probable reason for this is that the adducts are of a different structure: piperazine acts as a bidentate ligand between two different cobalt(II) ions while bipyridine acts as a bidentate ligand on the same cobalt(II) ion. Thus, it is not possible to compare these adducts. Morpholine is expected to be less basic than piperidine due to an inductive effect of substitution of one carbon atom in the ring of piperidine by the more electronegative oxygen atom. This is observed for adducts of these two ligands with arsenic trihalides [34]. The inverse order observed here could be due to the contribution of hydrogen bonding between carbon atoms (from acetylacetonate ions) and oxygen atoms (from morpholine ligands).

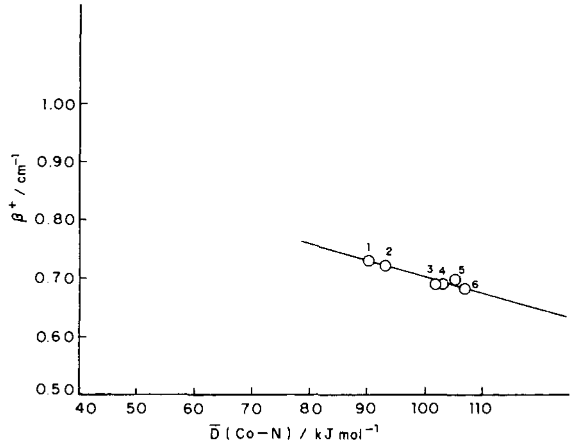

Fig. 2. Correlation of β^+ values with $\bar{D}_{(Co–N)}$ values for the adducts of Co(AcAc)$_2$ with: (1) – Pipd, (2) – Py, (3) – 3-cyanopy, (4) – 4-cyanopy, (5) – Morph and (6) – Quin.

Comparing the ligand field parameter D_q with the thermochemical parameter $\bar{D}$ (Co–N) for the adducts of the same stoichiometry, we observed for the adducts of Pipd, Py, β-Pico, γ-Pico and 3-cyanopy that the D_q values increase with the increase of $\bar{D}$ (Co–N) values, indicating that the splitting of the *d* orbital of Co(II) ion is favoured by stronger Co–N bonds (Fig. 1). Comparing β^+ values with $\bar{D}$ values, we observed for the adducts of Pipd, Py, 3-cyanopy, 4-cyanopy, Morph, and Quin, that the β^+ values decrease with the increase of the $\bar{D}$ (Co–N) values, indicating that the covalance of the *d* orbital of Co(II) ion is higher as the Co–N bond is stronger (Fig. 2).

In conclusion Co–N bonds in adducts of Co(II) acetylocetonate are weaker than As–N bonds in adducts formed by the same heterocyclic bases with arsenic trihalides [34,37,42].

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