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Thermochemistry of Adducts of Bis(2,4-pentanedionato)zinc with Heterocyclic Amines

P. Oliver Dunstan

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

The adducts $Zn(AcAc)_2 \cdot nL$ [where 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); $n = 1$ or $^3/_2$; AcAc = acetylacetonate] were synthesized and characterized by melting points, elemental analysis, thermal studies, and infrared spectroscopy. From calorimetric studies in solution, the mean standard enthalpies of the zinc−nitrogen bonds were determined.

Introduction

Heterocyclic bases are known to form coordination compounds with β-diketonates of divalent 3d electron elements (Mohapatra and Romana Rao, 1970; Pellacani et al., 1973). However, there is a lack of information about the enthalpies of the transition element−nitrogen bonds in these kind of compounds. Adducts of zinc acetylacetonate with heterocyclic amines were synthesized with the purpose of determining the mean strength of the Zn−N bonds. The effect of introducing a methyl group into the pyridine ring over the energy of the Zn−N bond is also studied. Correlations between the bond energies and the basicity of ligands are established.

Experimental Section

Chemicals. Zinc acetylacetonate was prepared by the method of Rudolph and Henry (1967). The compound was recrystallized from methanol and dehydrated under reduced pressure at 378 K. The purity of $Zn(AcAc)_2$ (AcAc = acetylacetonate) was of 99−100% as chemical analyses showed. Piperazine (pipz; Aldrich; 99%) was purified by recrystallization from methanol (mp = 107−8 °C). Morpholine (morph; Aldrich; 99%), piperidine (pipd; RPE Analyticals, Carlo Erba; 99%), pyridine (py; Reagen, r.a.), 3-methylpyridine (β-pico; Backer; 99%), 4-methylpyridine (γ-pico; Backer; 99%), and quinoline (quin; Aldrich; 98%) were all purified by distillation using an efficient column and stored over Linde 4 Å molecular sieves (bp = 123−4, 111−2, 139−40, 140−1, 111−2/(20 mmHg), and 103−4 °C, respectively).

3-Cyano- (3-cyanopy; Aldrich; 98%) and 4-cyanopyridine (4-cyanopy; Aldrich; 98%) were purified by recrystallization from methanol (mp = 49−50 and 77−8 °C, respectively). 2,2′-Bipyridine (bipy; Aldrich; 99%) was purified by recrystallization from ethanol according to the method described by Gallagher et al. (1978; mp = 193−4 °C). Solvents used in the synthesis of the adducts were purified by distillation and stored over Linde 4 Å molecular sieves.

Adducts Synthesis. The adducts were prepared by the reaction of zinc acetylacetonate and ligands in solution. A typical procedure is given below.

Zinc Acetylacetonate Pyridine. To a solution of 1.0 g of $Zn(AcAc)_2$ (3.79 mmol) in 0.40 dm^3 of hot methanol, 0.61 cm^3 of pyridine (7.58 mmol) was added slowly and dropwise with stirring. The solution was evaporated to about 30 cm^3 of volume, cooled to room temperature and placed in the refrigerator for several hours. The solid that formed was filtered off, washed with 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 molar ratio donor/acceptor of 2/1. Only in the case of piperidine the zinc acetylacetonate was dissolved in 20 cm^3 of the warm ligand. For solid ligands a solution of the ligand in hot methanol was added to the hot methanol solution of $Zn(AcAc)_2$. The purity of the adducts was of 99.5−100% as their chemical analysis showed.

Analytical Section. Carbon, hydrogen, and nitrogen contents were determined by microanalytical procedures. The zinc content was determined by complexometric titration with 0.01 M EDTA solution (Flaschka, 1964) of the aqueous solution of adduct samples.

Spectra. Infrared spectra were obtained using samples of the adducts or ligands in a KBr matrix in the region 400−4000 cm^{-1} using a Perkin-Elmer 1600 series FTIR spectrophotometer. For liquid ligands, a film of the ligand sandwiched between NaCl plates was used.

Thermal Studies. These were made under a argon atmosphere using a Du Pont 951 TG Analyzer, with samples varing in mass from 4 to 7 mg (TG-DTG) and from 2 to 6 mg (DSC) and a heating rate of 10 K min^{-1}. The temperature ranges were 298−1214 K (TG-DTG) and 298−673 K (DSC). TG calibration for weight was made using calcium oxalate as a standard. TG calibration for temperature was made using metallic aluminum as a standard (mp = 660.37 °C). DSC calibration was made using metallic indium as a standard (mp = 156.73 °C, $\Delta_s^l H^\theta = 28.4$ J g^{-1}).

Calorimetric Measurements. All the solution calorimetric determinations were made in a LKB 8700-1 precision calorimeter. The accuracy of the calorimeter was obtained by determining the heat of dissolution of tris(hydroxymethylamino)methane in 0.1 mol dm^{-3} hydrochloric acid. The result (-29.78 ± 0.03 kJ mol^{-1}) is in agreement with the value recomended by IUPAC (Henrigton, 1974) of -29.763 ± 0.003 kJ mol^{-1}. The uncertainty intervals are twice the standard deviations of the means

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Table 1. Melting Points, Yields, Appearance, and Analytical Data of the Adducts

				% C		% H		% N		zinc	
compd	yield/%	T_m[a] K	appearance[b]	calcd	found	calcd	found	calcd	found	calcd	found
$Zn(AcAc)_2$	21	439	wh cr	45.57	46.09	5.35	4.99			24.80	24.50
$Zn(AcAc)_2 \cdot {}^3/_2(morph)$	64	370−3	l ye pw	48.74	48.38	7.03	6.97	5.33	5.18	16.58	16.58
$Zn(AcAc)_2 \cdot py$	33	400	wh cr	52.57	52.09	5.59	5.41	4.09	3.95	19.08	19.08
$Zn(AcAc)_2 \cdot \beta$-pico	38	401−3	wh cr	53.87	53.54	5.93	5.86	3.93	3.77	18.33	18.20
$Zn(AcAc)_2 \cdot \gamma$-pico	24	431−3	wh cr	53.87	53.50	5.93	5.82	3.93	3.94	18.33	18.08
$Zn(AcAc)_2 \cdot bipy$	38	455−8	l ye pw	57.23	56.90	5.28	5.16	6.67	6.71	15.57	15.27
$Zn(AcAc)_2 \cdot {}^3/_2(quin)$	67	433	wh pw	61.72	61.40	5.40	5.23	4.59	4.45	14.29	14.31

[a] Melting with decomposition. [b] Key: wh, white; ye, yellow; cr, crystals; pw, powder; l, light.

Table 2. IR Spectral Data (cm^{-1})[a]

				ligand bands							
compd	ν_{C-O}	ν_{C-C}	ν_{Zn-O}	ν_{N-H}	ν_{C-C}	ring	ν_{C-O-C}	δ_{H-N-C}	α_{C-C-C}	$ø_{C-C}$	new bands
$Zn(AcAc)_2$	1606 vs	1521 vs	557 m								
morph				3320 m	1425 s		1097 s	889 m 835 s			
$Zn(AcAc)_2 \cdot {}^3/_2(morph)$	1593 vs	1512 vs	545 m	3293 w			1105 s	893 s			
py					1573 sh				584 s	431 m	
$Zn(AcAc)_2 \cdot py$	1601 vs	1526 vs	556 m		1585 vs				639 m	420 s	1220 m
β-pico					1572 sh 1558 s	1206 s					
$Zn(AcAc)_2 \cdot \beta$-pico	1584 vs	1520 vs	556 m		no	1222 m					706 m
γ-pico					1585 s 1545 s	1206 s					
$Zn(AcAc)_2 \cdot \gamma$-pico	1593 vs	1520 vs	557 m		no	1228 m					726 m
bipy					1578 vs	1452 vs			619 s	423 m	
$Zn(AcAc)_2 \cdot bipy$	1600 vs	1514 vs	548 m		1578 vs	1456 vs			652 m	417 m	1307 s 769 m
quin					1620 s	1448 s				521 s	
$Zn(AcAc)_2 \cdot {}^3/_2(quin)$	1583 vs	1519 vs	556 m		no	1444 s				490 m	1319 m

[a] Key: α, ring deformation in plane; ø, ring deformation out of plane; ν, stretching; δ, angular deformation; ring, ring breathing; no, not observed. Intensity of bands: vs, very strong; s, strong; m, medium; w, weak, sh, shoulder.

Table 3. Thermoanalytical Data of the Compounds

	mass lost %					
compd	calc	obs	temp range/K	species lost	DSC peak temp/K	ΔH/(kJ mol^{-1})
$Zn(AcAc)_2 \cdot {}^3/_2(morph)$	100	87.58	392−448	−1.5 morph−$Zn(AcAc)_2$	365	49.40
		12.29[a]			413	32.19
					515	7.85
$Zn(AcAc)_2 \cdot py$	100	84.67	392−435	− py−$Zn(AcAc)_2$	383[b]	38.40
		15.33[a]			420	3.82
					440	18.53
$Zn(AcAc)_2 \cdot \beta$-pico	100	90.15	379−459	− β-pico−$Zn(AcAc)_2$	398	39.27
		4.87	730−831		427	65.10
		4.98[a]				
$Zn(AcAc)_2 \cdot \gamma$-pico	100	91.21	420−452	− γ-pico−$Zn(AcAc)_2$	433	43.27
		8.78[a]			437	24.81
$Zn(AcAc)_2 \cdot {}^3/_2(quin)$	100	82.12	317−467	−1.5 quin−$Zn(AcAc)_2$.	333	10.23
		18.32[a]			439	47.61
					466	90.74
$Zn(AcAc)_2 \cdot bipy$	100	94.19	426−488	− $Zn(AcAc)_2$−bipy	370	76.78
		5.81[a]			477	29.94
					512	49.70

[a] Residue at 1215 K. [b] Two overlapping peaks.

of about five replicate measurements on each compound.

Each measurement was performed at 298.15 ± 0.02 K with a thin-walled ampule containing reactant being broken in a glass reaction vessel containing 100 mL of calorimetric solvent. Details of the measurement procedure, the apparatus, and data processing have already been described (Dunstan, 1992).

Results and Discussion

All adducts obtained were solids. Attempts to syntheze solid adducts of zinc acetylacetonate with piperazine, piperidine, 3-cyanopyridine, or 4-cyanopyridine only yielded products of indefinite stoichiometry. The capillary melting points, yields, colors, appearance, and analytical data are summarized in Table 1.

Infrared Spectra. The most important IR bands are reported in Table 2. The assignments of ν_{C-O} and ν_{C-C} in the region 1500−1600 cm^{-1} are based on the works of Pinchas et al. (1967) and Behnke and Nakamoto (1967). Two bands are observed in this region for the adducts. These bands are assigned to C−O (1583−1606 cm^{-1}) and C−C (1512−1526 cm^{-1}) stretching vibrations. The bands observed in the region (545−556 cm^{-1}) are assigned to Zn−O modes (West and Riley, 1958; Lippincott and Psellos, 1952). ν_{C-O}, ν_{C-C}, and ν_{Zn-O} shift to lower frequencies in the adducts relative to the uncoordinated zinc acetylacetonate. This indicates that the amines are bonded to the zinc ion. These shifts are much more marked than those observed for the formation of zinc acetylacetonate (Graddon and Schulz, 1965). Considerable shifts to lower frequencies

Table 4. Enthalpies of Dissolution at 298.15 K[a]

m/mg	10^6n/mol	Q_r/J	DH^θ_{diss}/(kJ mol^{-1})	m/mg	10^6n/mol	Q_r/J	ΔH^θ_{diss}/(kJ mol^{-1})
$Zn(AcAc)_2(s)$ + 1.2 M 25% HCl + MetOH [$\Delta_1 H^\theta$/(kJ mol^{-1}) = 25.20 ± 0.36]							
67.8	257.2	6.664	25.91	32.1	121.8	3.091	25.38
36.2	137.3	3.612	26.30	19.4	73.6	1.981	26.92
32.5	123.3	3.227	26.17	44.4	168.4	3.997	23.73
31.5	119.5	3.065	25.65	24.8	94.1	2.180	23.17
31.4	119.1	2.973	24.96	33.1	125.6	3.032	24.15
25.8	97.9	2.444	24.97	20.9	79.3	1.749	22.06
1.5 morph(l) + $Zn(AcAc)_2$ − 1.2 M 25% HCl + MetOH [$\Delta_2 H^\theta$/(kJ mol^{-1}) = −76.48 ± 1.67]							
17.1	196.3	−13.451	−68.33	21.2	243.3	−18.836	−77.26
19.2	220.4	−16.825	−76.36	27.2	312.2	−25.247	−80.90
36.3	416.6	−31.488	−75.59				
$Zn(AcAc)_2 \cdot 1.5$ (morph(s)) + 1.2 M 25% HCl + MetOH [$\Delta_3 H^\theta$/(kJ mol^{-1}) = −16.14 ± 0.93]							
26.0	65.9	−1.012	−15.35	46.9	119.0	−1.659	−13.95
55.3	140.3	−2.230	−15.90	55.0	139.5	−2.531	−18.14
1 py(l) + $Zn(AcAc)_2$ − 1.2 M 25% HCl + MetOH [$\Delta_2 H^\theta$/(kJ mol^{-1}) = −22.67 ± 0.82]							
19.9	252.2	−5.722	−22.68	10.6	134.0	−2.770	−20.67
23.3	294.6	−6.520	−22.13	9.5	120.0	−3.310	−27.69
4.2	53.1	−1.389	−26.35				
$Zn(AcAc)_2 \cdot$py(s) + 1.2 M 25% HCl + MetOH [$\Delta_3 H^\theta$/(kJ mol^{-1}) = 20.00 ± 0.63]							
19.9	57.1	1.258	22.05	42.2	121.0	2.335	19.30
27.9	80.0	1.763	22.04	48.5	139.1	2.714	19.52
β-pico(l) + $Zn(AcAc)_2$ − 1.2 M 25% HCl + MetOH [$\Delta_2 H^\theta$/(kJ mol^{-1}) = −19.50 ± 0.41]							
28.1	301.7	−6.148	−20.38	12.1	129.9	−2.261	−17.40
17.9	192.2	−3.516	−19.85	18.4	197.7	−3.866	−19.56
19.9	213.7	−4.179	−19.56	7.9	84.8	−1.610	−18.98
$Zn(AcAc)_2 \cdot \beta$-pico(s) + 1.2 M 25% HCl + MetOH [$\Delta_3 H^\theta$/(kJ mol^{-1}) = 28.06 ± 0.69]							
20.6	57.75	1.5722	27.23	5.3	14.86	0.4083	27.48
12.4	34.76	1.0287	29.59	8.8	24.67	0.7408	30.03
γ-pico(l) + $Zn(AcAc)_2$ − 1.2 M 25% HCl + MetOH [$\Delta_2 H^\theta$/(kJ mol^{-1}) = −26.96 ± 0.74]							
26.9	288.8	−7.564	−26.19	32.1	344.7	−9.057	−26.28
19.2	206.2	−5.721	−27.77	16.0	171.8	−4.378	−25.48
7.4	79.5	−2.608	−32.83				
$Zn(AcAc)_2 \cdot \gamma$-pico(s) + 1.2 M 25% HCl + MetOH [$\Delta_3 H^\theta$/(kJ mol^{-1}) = 25.30 ± 0.46]							
19.0	53.3	1.439	27.02	18.1	50.7	1.192	23.50
32.3	90.5	2.307	25.48	41.0	114.9	2.894	25.18
1.5 quin(l) + $Zn(AcAc)_2$ − 1.2 M 25% HCl + MetOH [$\Delta_2 H^\theta$/(kJ mol^{-1}) = −21.22 ± 0.25]							
15.4	119.2	−2.647	−22.22	34.3	265.6	−5.797	−21.80
11.6	89.8	−1.852	−20.60	10.2	78.9	−1.688	−21.29
48.3	373.9	−7.801	−20.86				
$Zn(AcAc)_2 \cdot 1.5$ quin(s) + 1.2 M 25% HCl + MetOH [$\Delta_3 H^\theta$/(kJ mol^{-1}) = 34.13 ± 2.52]							
18.9	41.3	1.727	41.79	10.0	21.9	0.732	33.48
45.9	100.4	3.587	35.74	30.3	66.3	1.824	27.53
bipy(s) + $Zn(AcAc)_2$ − 1.2 M 25% HCl + MetOH [$\Delta_2 H^\theta$/(kJ mol^{-1}) = 5.02 ± 0.23]							
7.9	50.6	0.282	5.58	26.3	168.4	0.808	4.80
16.3	104.4	0.591	5.67	11.5	73.6	0.337	4.58
$Zn(AcAc)_2 \cdot$bipy(s) + 1.2 M 25% HCl + MetOH [$\Delta_3 H^\theta$/(kJ mol^{-1}) = 49.51 ± 0.81]							
36.5	87.0	4.071	46.82	67.7	161.3	8.052	49.92
64.2	152.9	7.573	49.52	16.4	39.1	2.171	55.56

[a] Calorimetric solvent: 100 mL of 1.2 M 25% volume aqueous HCl in methanol.

of the ν_{N-H} of ligands after coordination are also observed. This is indicative of the coordination of morpholine through the nitrogen atom of its NH group (Ahuja, 1969; Ahuja and Garg, 1971). In the morpholine adduct, the positive shift of C−O−C stretching vibration with respect to free morpholine excludes the possibility of oxygen to zinc coordination (Ahuja, 1969). The change observed in the H−N−C deformation region (815−893 cm^{-1}) also affords evidence of the coordination of the nitrogen atom of the ligand (Sariego and Costamagna, 1971). The coordinated pyridine is distinguished from free pyridine by the presence in the adduct of a weak band at 1220 cm^{-1} and by the dislocation of bands at 1573, 584, and 431 cm^{-1} in free pyridine to higher frequencies in the adducts (Gill et al., 1961). This was observed in the spectra of the pyridine adduct. The infrared spectra of β- and γ-picoline show appreciable dislocations toward higher frequencies of the bands at 1545−1585 and 1206 cm^{-1} in the free ligands (Graddon and Watton, 1965; Gill and Kingdon, 1966). Only the dislocation of the last band is observed since the other two bands are covered by zinc acetylacetonate bands. The infrared spectra of the bipyridine adduct shows the appearance of new bands after coordination. Two new bands appear at 1307 and 769 cm^{-1}, both of which are absent in free bipyridine and are due to adduct formation (Sinha, 1964). The infrared spectra of the quinoline adduct show dislocation of several bands with respect to the free ligand. A new band is observed at 1319 cm^{-1} after coordination. The infrared data of the bipyridine and quinoline adducts can be interpreted in terms of the coordination of these ligands through the nitrogen atom to the zinc ion (Sinha, 1964; Mohapatra and Romana Rao, 1970).

Thermal Studies. The thermogravimetry (TG-DTG) of the adducts shows the loss of ligand and zinc acetylaceto-

Table 5. Summary of the Thermochemical Results

compd	$\Delta_r H^\theta$/ (kJ mol^{-1})	$\Delta_f H^\theta$/ (kJ mol^{-1})	$\Delta_{s,l}^{g} H^\theta$/ (kJ mol^{-1})	$\Delta_M H^\theta$/ (kJ mol^{-1})	$\Delta_D H^\theta$/ (kJ mol^{-1})	$\Delta_r H_{(g)}{}^\theta$/ (kJ mol^{-1})	$\bar{D}$(Zn−N)/ (kJ mol^{-1})
$Zn(AcAc)_{2(s)}$		−949.9 ± 2.2[a]	90 ± 10[a]				
$morph_{(l)}$		−170.2[b]	42.3[b]				
$py_{(l)}$		101.2 ± 0.7[c]	40.2[c]				
β-$pico_{(l)}$		61.9 ± 0.5[c]	44.4 ± 00[c]				
γ-$pico_{(l)}$		58.5 ± 1.1[c]	45.3 ± 0.4[c]				
$bipy_{(s)}$		216.4 ± 7.4[d]	81.93 ± 0.33[e]				
$quin_{(l)}$		141.22 ± 0.92[f]	59.32 ± 0.20[f]				
$Zn(AcAc)_2 \cdot {}^3/_2(morph(s))$	−35.14 ± 1.95	−1240.3 ± 3.1		−189 ± 10	98.6 ± 2.5	−146 ± 10	98 ± 7
$Zn(AcAc)_2 \cdot py(s)$	−17.47 ± 1.09	−866.2 ± 2.6		−148 ± 10	57.7 ± 1.1	−107 ± 10	107 ± 10
$Zn(AcAc)_2 \cdot \beta$-pico(s)	- 22.39 ± 0.89	- 910.4 ± 2.5		−156 ± 10	66.79 ± 0.9	−112 ± 10	112 ± 10
$Zn(AcAc)_2 \cdot \gamma$-pico(s)	−26.62 ± 0.82	−918.0 ± 2.6		−162 ± 10	71.9 ± 0.9	−117 ± 10	117 ± 10
$Zn(AcAc)_2 \cdot bipy(s)$	−19.29 ± 0.92	−752.8 ± 7.7		−191 ± 10	101.22 ± 0.98	−109 ± 10	55 ± 5
$Zn(AcAc)_2 \cdot {}^3/_2(quin(s))$	−30.15 ± 2.56	−768.2 ± 3.7		−209 ± 10	119.1 ± 2.6	−150 ± 10	100 ± 7

[a] Kakolowicz and Giera, 1983. [b] Dunstan, 1996. [c] Pedley and Rylance, 1970. [d] Airoldi et al., 1986. [e] Favour and Akasheh, 1985. [f] Steele et al., 1988.

nate together in one step. Only in the case of the β-picoline adduct are two steps of mass lost. The first step is the loss of ligand and pyrolisis of zinc acetylacetonate and the second is the decomposition of the residue of the pyrolysis of the zinc acetylacetonate. In all cases a residue is observed, probably carbon, coming from the pyrolysis of zinc acetylacetonate. The capillary melting points showed the decomposition of adducts on melting. They are unstable in the liquid phase. The DSC curves of the adducts, which are consistent with the TG data, showed several endothermic peaks due to elimination of the ligand and melting, elimination of ligand, melting, elimination of the ligand and pyrolysis of the zinc acetylacetonate, melting with elimination of the ligand and pyrolysis of zinc acetylacetonate or decomposition of the residues of the pyrolysis of acetylacetonate. Table 3 lists the thermoanalytical data of the adducts.

Calorimetric Measurements. The standard enthalpies of dissolution of zinc acetylacetonate, ligands, and adducts were obtained as previously reported (Dunstan, 1992). The standard enthalpy of reaction ($\Delta_r H^\theta$) can be determined for reaction 1. These standard enthalpy changes were obtained

$$\mathrm{Zn(AcAc)_2(s)} + n\mathrm{L(s,l)} = \mathrm{Zn(AcAc)_2{\cdot}}n\mathrm{L(s)};\quad \Delta_r H^\theta \qquad (1)$$

through the standard enthalpy of reactions 2−5 in solution.

$$\mathrm{Zn(AcAc)_2(s)} + \text{calorimetric solvent} = \text{solution A};\quad \Delta_1 H^\theta \qquad (2)$$

$$n\mathrm{L(s,l)} + \text{solution A} = \text{solution B};\quad \Delta_2 H^\theta \qquad (3)$$

$$\mathrm{Zn(AcAc)_2{\cdot}}n\mathrm{L(s)} + \text{calorimetric solvent} = \text{solution C};\quad \Delta_3 H^\theta \qquad (4)$$

$$\text{solution B} = \text{solution C};\quad \Delta_4 H^\theta \qquad (5)$$

The application of Hess' law to the series of reactions 2−5 gives $\Delta_r H^\theta$. Thus, $\Delta_r H^\theta = \Delta_1 H^\theta + \Delta_2 H^\theta - \Delta_3 H^\theta$ since the final B and C solutions are equivalent and $\Delta_4 H^\theta = 0$. Using appropriate thermochemical cycles and applying Hess law, the standard enthalpies of the following reactions were obtained.

$$\mathrm{Zn(AcAc)_2(g)} + n\mathrm{L(g)} = \mathrm{Zn(AcAc)_2{\cdot}}n\mathrm{L(s)};\quad \Delta_M H^\theta$$

$$\Delta_M{}^\theta = \Delta_r H^\theta - \Delta_s^g H^\theta(\mathrm{Zn(AcAc)_2}) - n\Delta_{s,l}^g H^\theta(\mathrm{L})$$

$$\mathrm{Zn(AcAc)_2{\cdot}}n\mathrm{L(s)} = \mathrm{Zn(AcAc)_2(s)} + n\mathrm{L(g)};\quad \Delta_D H^\theta$$

$$\Delta_D H^\theta = n\Delta_{s,l}^g H^\theta(\mathrm{L}) - \Delta_r H^\theta$$

$$\mathrm{Zn(AcAc)_2{\cdot}}n\mathrm{L(g)} = \mathrm{Zn(AcAc_2(g)} + n\mathrm{L(g)};\quad \Delta_r H^\theta(\mathrm{g})$$

$$\Delta_r H^\theta(\mathrm{g}) = -\Delta_s^g H^\theta(\mathrm{Zn(AcAc)_2}) - n\Delta_{s,l}^g H^\theta(\mathrm{L}) + \Delta_r H^\theta + \Delta_{s,l}^g H^\theta(\mathrm{L})$$

The $\Delta_r H^\theta$(g) values can be used to calculate the standard enthalpy of the zinc−nitrogen bond ($\bar{D}$(Zn−N)), being equal to $-\Delta_r H^\theta(\mathrm{g})/n$. Because $Zn(AcAc)_2$ exists as a polymer in the solid state (Fackler, 1996), a hypothetical monomer for the calculation of the standard enthalpy of dissolution of $Zn(AcAc)_2(s)$ + solvent → $Zn(AcAc)_2(s)$, $\Delta_1 H^\theta$ was assumed. Table 4 gives the values obtained for the enthalpies of dissolution of zinc acetylacetonate ($\Delta_1 H^\theta$), the ligand into the solution of $Zn(AcAc)_2$ ($\Delta_2 H^\theta$), and 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 (Dunstan and dos Santos, 1989; Fackler, 1996), 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 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 $\Delta_1 H^\theta$(g) values were used to calculate the standard enthalpies of the Zn−N bonds (Dunstan and dos Santos, 1989). Table 5 lists the values obtained for all of 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 1 mol of ligand (Dunstan, 1992, 1994; Dunstan and dos Santos, 1989) 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.

On the basis of the $\Delta_r H^\theta$ values for the adducts of the same stoichiometry, we obtain the following basicity sequence: γ-pico > β-pico > py and morph > quin. The same sequence except for the inversion between morph and quin is obtained using the $\bar{D}$(Zn−N) values as the stronger bond is formed with the stronger base. The expected order for pyridine and derivatives would be γ-pico > β-pico > py due to an inductive effect from substitution of one hydrogen atom in the pyridine ring by the electronic donator methyl group in β- or γ-picoline. This causes the increase of the electronic density available for bonding on the nitrogen atom of the ring relative to pyridine. The inductive effect in p-substitution is stronger than in m-substitution. Between morph and quin, the latter is expected to be a better base as the electronic density on the nitrogen atom is improved by the electronic density of the aromatic rings.

Summing up, the $\bar{D}$(Zn−N) and other thermochemical parameters data indicate that the Zn−N bond is stronger as we go in the sequence py < β-pico < γ-pico and morph < quin. The substitution of one hydrogen atom in the pyridine ring by the electronic donator methyl group causes the increase of Zn−N bond energy in the cases of γ-picoline and β-picoline, both relative to the not substituted pyridine, being stronger in the p-substitution as it would be expected.

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