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Thermochemistry of adducts of manganese(II) and copper(II) pentane-2,4-dionate with heterocyclic amines

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Abstract

The compounds [M(pd)$_2$(L)] (where M is manganese(II) or copper(II); pd is pentane-2,4-dionate; and L is piperazine (pipz), 4-cyanopyridine (4-cyanopy), quinoline (quin) or 2,2′-bipyridine (bipy)) were synthesized and characterized by elemental analysis, melting points, thermal studies and electronic and IR spectroscopy. The enthalpies of dissolution of adducts, metal pentane-2,4-dionate 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 reaction in the gaseous phase ($\Delta_r H^\theta$(g)). The mean standard bond dissociation enthalpies of the manganese–nitrogen and copper–nitrogen bonds have been determined. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Adducts of pentane 2,4-dionate chelates of divalent first transition series metals with several heterocyclic amines are reported in the literature [1–7]. Although there is extensive thermochemical data available for several metallic pentane-2,4-dionate chelates, including metal–oxygen bond dissociation enthalpies [8,9], there is a lack of information about the metal–nitrogen bond dissociation enthalpies in adducts formed by these chelates. Recently, we determined the values of these enthalpies for the adducts of Co(II), Ni(II) or Zn(II) pentane-2,4-dionate with heterocyclic amines [10–12]. In this work, we synthesized adducts of manganese(II) and copper(II) pentane-2,4-dionates with heterocyclic amines with the intention of measuring the mean metal–nitrogen bond dissociation enthalpies in these adducts. We establish correlations between the bond dissociation enthalpies obtained with the standard enthalpies for the acid/base reactions, as well correlations between the standard enthalpies of formation of the gaseous adducts with the metal atomic number, and compare the values obtained for these enthalpies with the values obtained for Co(II), Ni(II) and Zn(II) pentane-2,4-dionate adducts of the same ligands.

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2. Experimental

2.1. Chemicals

Mn(II) pentane-2,4-dionate was synthesized by the Charles method [13]. The yellow chelate was dehydrated by heating in vacuo at 398 K for several hours. The results of the chemical analysis of the resulting tan product were: Mn, 21.52; C, 47.88; H, 5.49 mass% (theoretical: Mn, 21.70; C, 47.45; H, 5.57).

Cu(II) pentane-2,4-dionate was synthesized according to the method of Charles and Pawlikowsky [14]. The blue product was recrystallized from methanol and dried at 408 K during several hours. The results of the chemical analysis were: Cu, 24.51; C, 45.90; H, 5.37 mass% (theoretical: Cu, 24.27; C, 45.89; H, 5.39).

Piperazine (99%, Aldrich) was purified by recrystallization from methanol (mp 107–108°C). 2,2′-bipyridine (99%, Aldrich) was purified by recrystallization from ethanol according to the method described by Gallagher et al. [15] (mp 193–194°C). 4-Cyanopyridine (98%, Aldrich) was purified by recrystallization from methanol (mp 77–80°C). Quinoline (98%, Aldrich) was purified by distillation using an efficient column and stored over 4 Å molecular sieves (bp 111–112/20 mm Hg). Other solvents used 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 metal content was determined by complexometric titration with 0.01 M EDTA solution [16] of the aqueous solution of adducts. The melting points of the adducts were determined using a UNIMELT from Thomas Hover Company.

2.3. Adduct synthesis

The adducts were prepared by the reaction of Mn(II) pentane-2,4-dionate and ligands in solution or by the direct reaction of Cu(II) pentane-2,4-dionate with excess of ligands. A typical procedure is given below.

To a solution of 1.0 g of $Mn(pd)_2$ (4.0 mmol) in 20 ml of methanol, 1.00 ml of quinoline (8.5 mmol) was added slowly and dropwise with stirring. The mixture was cooled in a freezer and the solid formed was filtered under nitrogen and washed with three portions of 20 ml of petroleum ether. The product was dried for several hours in vacuo and stored in a desiccator over calcium chloride.

2.4. Infrared spectra

Infrared spectra were obtained for solid samples in KBr matrix. For liquid samples 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 analysis

TG measurements were made in an argon atmosphere using a Du Pont 951 TG analyser, with samples varying in mass from 2.14 to 8.74 mg (TG–DTG) and from 1.46 to 2.14 mg (DSC) and a heat rate of 10 K min^{-1} in the 298–1214 K range (TG–DTG) and 298–673 K (DSC). The TG calibration for mass was done mechanically. 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 (mp 156.73°C, $\Delta_{\mathrm{c}}^{1}H^{\theta}=28.4$ J g^{-1}).

2.6. Calorimetric measurements

Solution calorimetric determinations were carried out using an LKB 8700-1 precision calorimeter as described previously [17]. The measurements were performed by dissolving samples of 3.9–129 mg of the adducts or metal pentane-2,4-dionate in a 1:3 (v/v) mixture of aqueous HCl 1.2 M and methanol. The ligands were dissolved in the solution of metal pentane-2,4-dionate maintaining a stoichiometric molar ratio. The accuracy of the calorimeter was checked by determining the heat of dissolution of tris(hydroxymethyl)aminomethane in 0.1 mol dm^{-3} HCl. The mean result (-29.78 ± 0.03 kJ mol^{-1}) is in agreement with the value recommended by IUPAC [18] (-29.763 ± 0.003 kJ mol^{-1}).

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

Compound	Yield	Melting point[a] (°C)	Appearance	C		H		N		M	
				Calculated	Found	Calculated	Found	Calculated	Found	Calculated	Found
[Mn(pd)2(pipz)]	50	237–9	Light, yellow, powder	49.56	49.15	7.13	7.14	8.26	7.98	16.19	16.10
[Mn(pd)$_2$(4-cyanopy)]	28	250–2	Light yellow powder	53.79	53.54	5.08	4.99	7.84	7.75	15.38	15.26
[Mn(pd)$_2$(bipy)]	31	245–7	Light yellow powder	58.68	58.48	5.42	5.29	6.84	6.76	13.42	13.40
[Cu(pd)$_2$(quin)]	27	275–7	Light blue crystals	58.38	58.20	5.41	5.25	3.58	3.50	16.25	16.14

[a] Melting point with decomposition.

2.7. Electronic spectra

Electronic spectra of the solid adducts in the 350–2000 nm region 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 ranged from 27 to 50%. In methanol solution, reaction of Mn(II) pentane-2,4-dionate with morpholine, piperidine, pyridine, 3-methylpyridine, 4-methylpyridine, 3-cyanopyridine and quinoline did not produce an adduct. Cu(II) pentane-2,4-dionate only produced the adduct of quinoline. 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 assigments of $\nu_{(\text{C–O})}$, $\nu_{(\text{C–C})}$ in the region 1600–1500 cm^{-1} region are based on the works of Pinchas et al. [19] and Bennke and Nakamoto [20]. Two bands are observed in the 1600–1500 cm^{-1} region for the adducts. These bands are assigned to C–O (1608–1577 cm^{-1}) and C–C (1534–1513 cm^{-1}) stretching vibrations. The bands in the 654–438 cm^{-1} region are assigned to Mn–O and Cu–O modes [21–23]. The $\nu_{(\text{C–O})}$, $\nu_{(\text{C–C})}$ and $\nu_{(\text{Me–O})}$ bands shift to lower frequencies in the adducts relative to the uncoordinated M(II) pentane-2,4-dionate, thus indicating that the ligands are bonded to the metallic ion [2]. Considerable shift to lower frequencies of $\nu_{(\text{N–H})}$ band of piperazine after coordination is also observed. This is indicative of coordination of piperazine through the nitrogen atom of their NH group [21,22]. The infrared

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

Compound	$\nu_{(\text{C–O})}$	$\nu_{(\text{C–C})}$	$\nu_{(\text{M–O})}$	Ligand bands						
				$\nu_{(\text{N–H})}$	$\nu_{(\text{C–C})}$	$\nu_{(\text{C–N})}$	Ring	$\delta_{(\text{H–N–C})}$	$\phi_{(\text{C–C})}$	New bands
Mn(pd)$_2$	1605 vs	1506 vs	659 m							
Pipz				3328 m	1461 s			861 m, 815 s		
[Mn(pd)$_2$(pipz)]	1608 vs	1515 vs	651 m	3210 m	1464 m			886 m		
4-Cyanopy						2236 s	1216 s			
[Mn(pd$_2$)(4-cyanopy)]	1602 vs	1513 vs	654 m			2238 s	1252 s			
Bipy					1576 s		990 m		751 vs	
[Mn(pd)$_2$(bipy)]	1606 vs	1522 vs	648 m		1580 vs		n.o.		777 vs	1350 m, 737 m
Cu(pd)$_2$	1577 vs	1534 vs	454 m							
Quin					1602 s		1031 m			
[Cu(pd)$_2$(puin)]	1581 vs	1523 vs	438 m		n.o.		n.o.			598 m

[a] ν: stretching; δ: angular deformation; ϕ: ring deformation out of plane; ring: ring breathing; n.o.: not observed; intensity of bands — vs: very strong; s: strong; m: medium.

spectra of the adduct of 4-cyanopyridine shows an appreciable shift towards higher frequencies of the band at 1216 cm^{-1} in the free ligand. Shifts to higher frequencies of the band assigned to the group CN is also observed. This is indicative of coordination of the ligand through the nitrogen atoms [23–25]. The infrared spectra of the bipyridine adduct shows the appearance of new bands after coordination at 1350 and 737 cm^{-1}, both of which are absent in free bipyridine and are due to adduct formation [26]. The infrared spectra of the quinoline adduct shows a shift of several bands with respect to the free ligand. A new band appears after coordination at 598 cm^{-1}. The infrared data of bipyridine and quinoline adducts can be interpreted in terms of coordination of these ligands through the nitrogen atom to the metal pentane-2,4-dionate [5,26].

3.2. Thermal analysis

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

I. $[\mathrm{Mn(acac)_2(L)}] \rightarrow$ pyrolysis
II. $[\mathrm{Mn(acac)_2(4\text{-}cyanopy)}] \rightarrow \mathrm{Mn(acac)_2} + 4\text{-cyanopy}$
$\mathrm{Mn(acac)_2} \rightarrow$ pyrolysis
III. $[\mathrm{Cu(acac)_2(quin)}] \rightarrow [\mathrm{Cu(acac)_2(quin)_{0.3}}] + 0.7\,\mathrm{quin}$
$[\mathrm{Cu(acac)_2(quin)_{0.3}}] \rightarrow$ pyrolysis

The adducts of piperazine and bipyridine followed Process I with one-step mass lost that is due to the pyrolisis of the adduct, leaving a residue that is probably a mixture of carbon and metal. The DSC curves of these adducts are consistent with TG–DTG data. They present an endothermic peak at 488 K due to the melting and pyrolysis of the adduct of piperazine, endothermic peaks at 344 and 433 K are due to partial separation of bipyridine. An endothermic peak at 514 K is due to melting and pyrolysis of manganes(II) pentane-2,4-dionate.

The adduct of 4-cyanopyridine followed Process II with the mass lost in two steps: the first with the elimination of the ligand and the second with the pyrolysis is of the manganes(II) pentane-2,4-dionate leaving a residue that is probably a mixture of metal and carbon. The DSC curve of the adduct is consistent with the TG–DTG data. It shows an endothermic peak at 425 K due to the elimination of 4-cyanopyridine and an endothermic peak at 530 K due to the melting and decomposition of manganese(II) pentane-2,4-dionate.

The adduct of quinoline followed Process III with the elimination of part of the ligand in a first step of mass lost. In a second step of mass lost is eliminated the rest of the ligand and products of the decomposition of the Cu(II) pentane-2,4-dionate. The DSC curve is consistent with the TG–DTG data. It shows an endothermic peak at 369 K due to the partial elimination of the ligand and an endothermic peak at 427 K due to the elimination of the rest of the ligand and

Table 3
Thermoanalytical data of the compounds

Compound	Mass lost (%)		TG temperature range (K)	Species lost	DSC peak temperature (K)	Enthalpy (kJ mol^{-1})
	Calculated	Observed				
$[\mathrm{Mn(pd)_2(pipz)}]$	79.1	75.0	503–546	$-\mathrm{Mn(pd)_2(pipz)}$[a]	488	39.71
	20.9	23.0[b]				
$[\mathrm{Mn(pd)_2(4\text{-}cyanopy)}]$	29.1	27.7	378–410	–4-Cyanopy	425	81.14
	46.5	53.3	562–546	$-\mathrm{Mn(pd)_2}$[a]	530	25.67
	24.3	24.0[b]				
$[\mathrm{Mn(pd)_2(bipy)}]$	82.7	81.8	464–530	$-\mathrm{Mn(pd)_2(bipy)}$[a]	344	67.87
	17.3	15.7[b]			433	31.98
					514	43.43
$[\mathrm{Cu(pd)_2(quin)}]$	23.1	22.5	349–372	–0.7quin	369	9.44
	76.9	73.9	372–493	$-0.3\mathrm{quin}-\mathrm{Cu(pd)_2}$	427	16.67
		3.6[b]			541	96.64

[a] Pyrolysis.
[b] Residue at 1215 K.

Table 4
Band maximum assignments (cm^{-1}) for the compounds

Compound	Band maximum
$[Mn(pd)_2(pipz)]$	28796
$[Mn(pd)_2(4\text{-cyanopy})]$	26666
$[Mn(pd)_2(bipy)]$	27469
$[Cu(pd)_2(quin)]$	15417

pyrolysis of the Cu(II) pentane-2,4-dionate. Table 3 lists the thermoanalytical data of the adducts.

3.3. Electronic spectra

Table 4 contains the band maxima assigments for the adducts. Since only forbidden bands can be observed in the electronic spectra of high-spin Mn(II) compounds, it is impossible to determine accurately the ligand-field parameters Dq, B and β^+ [27]. It is, however, possible to deduce the local symmetry of the manganese ion, which is pseudo-octahedral [27] from the shapes, intensities and relative positions of the absorption bands. For the Cu(II) adduct, electronic spectra show a single, rather broad band. Intensity and position correspond with those observed for penta-coordinated Cu(II) [1].

3.4. Calorimetric measurements

The standard enthalpies of dissolution of manganese(II) or copper(II) pentane-2,4-dionate, ligands and adducts were obtained as previously described [11]. The standard enthalpies of dissolution were obtained according with the standard enthalpies of reactions 1–4 in solution:

$$\mathrm{M(pd)_{2(s)}} + \text{calorimetric solvent} \rightarrow \text{solution A};\quad \Delta_1 H^\theta$$

$$\mathrm{L_{(s,1)}} + \text{solution A} \rightarrow \text{solution B};\quad \Delta_2 H^\theta \qquad (2)$$

$$\mathrm{[M(pd)_2(L)]_{(s)}} + \text{calorimetric solvent} \rightarrow \text{solution C};\quad \Delta_3 H^\theta$$

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

The application of Hess' law to the series of reactions 1–4 gives the standard enthalpies of the acid/base reactions ($\Delta_r H^\theta$), according to the reaction (5):

$$\mathrm{M(acac)_{2(s)}} + \mathrm{L_{(s,1)}} \rightarrow \mathrm{[M(acac)_2(L)]_{(s)}};\quad \Delta_r H^\theta = \Delta_1 H^\theta + \Delta_2 H^\theta - \Delta_3 H^\theta$$

since the final B and C solution equivalent and $\Delta_4 H^\theta=0$.

Table 5 gives the values obtained for the enthalpies of dissolution of manganese(II) or copper(II) pentane-2,4-dionate ($\Delta_1 H^\theta$), ligands into the solution of $M(pd)_2$ ($\Delta_2 H^\theta$) and of the adducts ($\Delta_3 H^\theta$). Uncertainty intervals given in this table are twice the standard deviations of the mean of five replicate measurements on each compound. From the values obtained for the standard enthalpies of dissolution and using appropriate thermochemical cycles [28], the following thermochemical parameters were determined: 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

Table 5
Standard molar enthalpy change ($kJ\ mol^{-1}$) of solution-reaction at 298.15 K

Compound	Calorimetric solvent[a]	No. of experiments	$\Delta_i H^\theta$ ($kJ\ mol^{-1}$)
$Mn(pd)_2$	HCl 1.2 M–methanol	6	(i=1) −25.81±1.38
Pipz	1:1 $Mn(acac)_2$–HCl 1.2 M–methanol	4	(i=2) −57.88±1.05
$[Mn(pd)_2(pipz)]$	HCl 1.2 M–methanol	5	(i=3) −51.95±1.85
4-Cyanopy	1:1 Mn(acac)2–HCl 1.2 M–methanol	4	(i=2) 20.24±0.67
$[Mn(pd)_2(4\text{-cyanopy})]$	HCl 1.2 M–methanol	5	(i=3) 10.12±0.56
Bipy	1:1 $Mn(acac)_2$ –HCl 1.2 M–methanol	4	(i=2) 10.71±0.49
$[Mn(pd)_2(bipy)]$	HCl 1.2 M–methanol	4	(i=3) 4.95±0.10
$Cu(pd)_2$	HCl 1.2 M–methanol	4	(i=1) 46.19±1.30
Quin	1:1 $Cu(acac)_2$–HCl 1.2 M–methanol	5	(i=2) 62.80±1.55
$[Cu(pd)_2(quin)]$	HCl 1.2 M–methanol	6	(i=3) −16.57±0.40

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

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

Compound	$\Delta_r H^\theta$	$\Delta_f H^\theta$	$\Delta_s^g H^\theta$ or $\Delta_l^g H^\theta$	$\Delta_M H^\theta$	$\Delta_D H^\theta$	$\Delta_r H^\theta$(g)	$\langle \overline{D} \rangle$(M−N)
$Mn(pd)_{2(s)}$		-1048.1 ± 2.2^a	88.7^a				
$Cu(pd)_{2(s)}$		-784.8 ± 2.2^a	109.6^a				
$Pipz_{(s)}$		-45.6 ± 1.6^b	84.2^c				
4-Cyanopy$_{(s)}$		77.87 ± 2.3^d	46.7 ± 1.5^d				
$Bipy_{(s)}$		216.4 ± 7.4^e	81.93 ± 0.33^f				
$Quin_{(l)}$		141.22 ± 0.92^g	59.32 ± 0.20^g				
$[Mn(pd)_2(pipz)]_{(s)}$	-31.74 ± 2.54	-1125.44 ± 3.72		-204.6 ± 3.4	115.9 ± 2.7	-120.4 ± 3.5	60.2 ± 1.8
$[Mn(pd)_2(4\text{-cyanopy})]_{(s)}$	-15.69 ± 1.57	-1222.8 ± 4.7		-188.0 ± 4.3	99.3 ± 3.8	-104.41 ± 5.6	72.2 ± 2.8
$[Mn(pd)_2(bipy)]_{(s)}$	-20.05 ± 1.47	-851.75 ± 7.9		-190.7 ± 2.5	101.98 ± 1.51	-108.8 ± 2.5	54.4 ± 1.3
$[Cu(pd)_2(quin)]_{(s)}$	-33.18 ± 2.06	-676.7 ± 3.2		-202.1 ± 2.1	92.5 ± 2.1	-142.8 ± 2.9	142.8 ± 1.5

[a] [27].
[b] [28].
[c] [29].
[d] [8].
[e] [30].
[f] [31].
[g] [32].

of the Lewis acid/base reactions in the gaseous phase ($\Delta_r H^\theta$(g)). The values of $\Delta_r H^\theta$(g) can be used to calculate the mean standard enthalpies of the Mn–N and Cu–N bonds. Table 6 lists the values obtained for all these thermochemical parameters. 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 [17,35], 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 pahse.

Based on the $\Delta_r H^\theta$ values for the adducts, we obtain the basicity order: pipz>bipy>4-cyanopy. By using the $\overline{D}_{(\mathrm{Mn-N})}$ values we obtain: bipy>pipz>4-cyanopy.The enthalpies for the process of complex formation in the gaseous phase from metal ions, pentane-2,4-dionate ion and ligands can be evaluated

$$M^{2+}_{(g)} + 2pd^{-1}_{(g)} + L_{(g)} \rightarrow [M(pd)_2(L)]_{(g)}, \quad \Delta_{fI} H^\theta \qquad (6)$$

being equal to

$$\Delta_{fI} H^\theta = \Delta_f H^\theta(\mathrm{adduct}_{(g)}) - \Delta_f H^\theta(M^{2+}_{(g)}) - 2\Delta_f H^\theta(pd^{-}_{(g)}) - \Delta_f H^\theta(L_{(g)})$$

Table 7 lists the values obtained for these enthalpies. The environment around the M(II) ions is pseudo-octahedral as it is formed by four oxygen atoms and two nitrogen atoms. Then, it is adequate to find corrections of the $\Delta_{fI} H^\theta$ values rather than correlations of the $\langle D \rangle$ (M–N) values. The correlation of the enthalpy changes of the ionic complex formation in

Table 7
Auxiliary data and the enthalpy changes of the ionic complex-formation process in the gaseous phase (kJ mol^{-1})

Species	$\Delta_r H^\theta$(g)	$\Delta_f H^\theta$(g)	$\Delta_{fI} H^\theta$
Mn^{2+}		2522.0 ± 0.1^a	
Co^{2+}		2841.7 ± 3.4^a	
Ni^{2+}		2930.5 ± 1.5^a	
Cu^{2+}		3054.5 ± 2.1^a	
Zn^{2+}		2781.0 ± 0.4^a	
pd^-		-217 ± 20^b	
Quin		200.54 ± 0.94^d	
Bipy		298.3 ± 7.4^c	
$[Mn(pd)_2(bipy)]$	-108.8 ± 2.5	-769.9 ± 8.1	-3156 ± 42
$[Co(pd)_2(bipy)]$	-93.1 ± 1.3^e	-597.7 ± 7.9	-3304 ± 42
$[Ni(pd)_2(bipy)]$	-103.0 ± 1.2^f	-619.9 ± 7.8	-3415 ± 41
$[Cu(pd)_2(bipy)]$	-142.8 ± 2.9	-617.5 ± 4.3	-3438 ± 40
$[Zn(pd)_2(bipy)]$	-109 ± 10^g	-671 ± 16	-3316 ± 44

[a] [36].
[b] [29].
[c] [32,33].
[d] [34].
[e] [10].
[f] [11].
[g] [12].

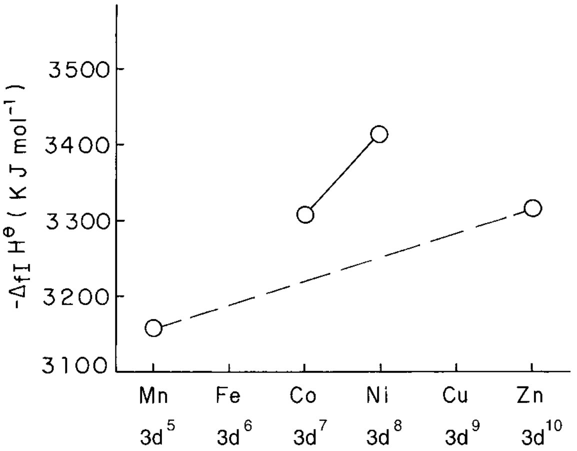

Fig. 1. Plot of enthalpy changes of complex formation in the gaseous phase from ionic components against d-electron configuration.

the gaseous phase ($\Delta_{\mathrm{fl}}H^{\theta}$) with the metal atomic number, shows part of the double periodic variation profile (Fig. 1). The same is observed considering $\langle D\rangle$(M–N)+$\langle D\rangle$(M–O) instead of $\Delta_{\mathrm{fl}}H^{\theta}$.

The mean bond dissociation enthalpies of the M–N bonds are weaker than the bond dissociation enthalpies of the M–O bonds in adducts of M(II) pentane-2,4-dionates with heterocyclic amines, as would be expected on the basis of the electronegative values of the oxygen atom and the chelate character of the pentane-2,4-dionate ion.

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