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Thermochemistry of adducts of some bivalent transition metal bromides with triphenylphosphine

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Abstract

The compounds [MBr$_m$(L)$_n$] (where M is Mn(II), Fe(II), Co(II), Ni(II), Cu(I) or Zn(II); L = triphenyphosphine (tpp); $m = 1$ or 2; $n = 1.5$, 2 or 3) were synthesized and characterized by melting points, elemental analysis, thermal analysis and electronic and IR spectroscopy. The enthalpies of dissolution of the adducts, metal(II) bromides and triphenylphosphine in methanol or in a solution of 10% (v/v) triethanolamine, 40% (v/v) acetonitrile and 50% (v/v) 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 bond dissociation enthalpies of the metal(II)–phosphorus bonds ($\bar{D}_{(M-P)}$) have been estimated.

Keywords: Metal bromides; Transition metals; Thermochemistry; Metal(II)–phosphorus bonds; Dissolution enthalpies

1. Introduction

Thermochemical parameters related to transition metal–phosphorus coordinated bonds do not exist in the literature. Although coordination compounds between metal(II) halides and triphenylphosphine are known, since the last half of the 20th century, they have not been the subject of any thermochemical study. Mostly they have been synthesized, characterized and some electronic studies have been made [1–8].

The thermodynamic properties of this kind of compound are important to help understand metal–phosphorus coordinated bonds. Also, the standard enthalpies of formation are important to characterize and understand their properties.

This paper reports the synthesis of complexes of some bromides of divalent 3d-elements with triphenylphosphine. They were synthesized with the purpose of obtaining several thermochemical parameters, to establish correlations among the obtained parameters and to determine the energy involved in the transition metal–phosphorus coordinated bond.

2. Experimental

2.1. Chemicals

Triphenylphosphine (BDH Chemicals Ltd.) was used as obtained. The anhydrous metal(II) bromides used in the preparation of the complexes were of reagent grade. Solvents used in the synthesis of the adducts were purified by distillation and stored over Linde 4 Å molecular sieves.

2.2. Analytical

Carbon and hydrogen contents were determined by microanalytical procedures. The metal contents were determined by complexometric titration with 0.01 M EDTA solution [9] of the aqueous solution of adduct samples. Bromide analysis

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was by gravimetry, using 0.1 M $AgNO_3$ solution, after the adducts had been dissolved in water [10]. The capillary melting points of the adducts were determined with a UNIMELT equipment from Thomas Hover.

2.3. Adduct synthesis

The adducts were prepared by reaction of MBr_2 dissolved in hot *n*-butanol ($FeBr_2$, $CoBr_2$ or $NiBr_2$), hot acetone ($CuBr_2$ or $ZnBr_2$) or hot tetrahydrofuran ($MnBr_2$) with a hot solution of triphenylphosphine in the same solvent used for dissolving the metal bromide. In all preparations a molar ratio salt/ligand of 1/2 was used. A typical procedure is given below.

To a solution of 2.20 g of $NiBr_2$ (10 mmol) dissolved in 40 mL of hot *n*-butanol, 5.30 g of triphenylphosphine (20 mmol) dissolved in 40 mL of hot *n*-butanol was added slowly and drop-wise with stirring. The mixture was refluxed for several hours. After cooling, the dark green crystals were filtered, washed with petroleum ether and dried for several hours in vacuum. The product was stored in a desiccator over calcium chloride.

2.4. Infrared spectra

Spectra were obtained with samples in KBr matrix for the adducts and ligand. A Perkin-Elmer 1600 series FTIR spectrophotometer in the 4000–400 cm^{-1} region was used.

2.5. Thermal studies

TG/DTG and DSC measurements were obtained in an argon atmosphere in a Du Pont 951 TG analyzer with samples varying in mass from 2.41 to 5.38 mg (TG/DTG) and from 2.05 to 6.43 mg (DSC) and a heating rate of 10 K min^{-1}in the 293–673 K (DSC) and 298–1253 K (TG/DTG) temperature ranges. TG calibration for temperature was made with metallic aluminum as a standard (mp = 660.37 °C) and the equipment carried out the calibration for mass automatically. The DSC calibration was made with metallic indium as a standard (mp = 165.73 °C, $\Delta_s{}^l H^\theta = 28.4\ J\ g^{-1}$).

2.6. Calorimetric measurements

Solution calorimetric determinations were done in an LKB 8700-1 precision calorimeter as described elsewhere [11]. The solution calorimetric measurements were performed by dissolving samples of 3.3–95.5 mg of the adducts or metal(II) bromides in 100 mL of methanol (or a mixture of triethanolamine–acetonitrile–methanol for the Co(II) compounds) and the triphenylphosphine in this latter 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 ($-29.78 \pm 0.03\ kJ\ mol^{-1}$) is in agreement with the value recommended by IUPAC ($-29.763 \pm 0.003\ kJ\ mol^{-1}$) [12].

3. Results and discussion

All the adducts obtained were solids. The yields, melting points, colors, appearance and analytical data are summarized in Table 1. The adduct $[CuBr(tpp)_3]$ was obtained from the reaction of $CuBr_2$ and triphenylphosphine in methanol. This was also observed by Tayin et al. [8]. The adduct of Fe(II) was obtained with a stoichiometric relation salt/ligand of 1/1.5 and not with the stoichiometry of 1/2 found in the literature [4].

3.1. Infrared spectra

The infrared spectra of the adducts show dislocation of some bands and the appearance of new ones when compared with the spectra of the free ligand. For the complexes, the band at 1089 cm^{-1} (x-sensitive *q*) observed in the free ligand is moved to higher frequencies and greatly increased in its intensity. A new band in the region 726–705 cm^{-1} (x-sensitive *r*) appeared after complexation. The strong band at 514 cm^{-1} in the free ligand, assigned to an out-of-plane ring deformation, moves 3–27 cm^{-1} to higher frequencies after complexation. These facts are taken as indicative of coordination of the triphenylphosphine to the metallic ions

Table 1
Yields in percentage on preparation, melting points and analytical data of the compounds

Compound	Yield (%)	mp[a] (K)	Appearance[b]	C (%)		H (%)		M (%)		Br (%)	
				Calculated	Found	Calculated	Found	Calculated	Found	Calculated	Found
$[MnBr_2(tpp)_2]$	82	534	li. ye. pw.	58.48	58.80	4.09	4.14	7.43	7.23	21.62	21.57
$[FeBr_2(tpp)_{1.5}]$	64	365	or. pw.	53.24	52.99	3.72	3.75	9.17	9.25	26.24	26.34
$[CoBr_2(tpp)_2]$	91	423	gre. bl. cr.	58.17	58.40	4.07	4.09	7.93	7.89	21.50	21.48
$[NiBr_2(tpp)_2]$	41	388	d. gre. cr.	58.19	58.03	4.07	3.98	7.90	7.92	21.51	21.54
$[CuBr(tpp)_3]$	34	438	wh. cr.	69.32	69.84	4.88	4.90	6.83	6.53	8.59	8.47
$[ZnBr_2(tpp)_2]$	62	492	wh. cr.	57.67	57.67	4.03	3.98	8.72	8.73	21.32	21.29

[a] Melting point with decomposition.

[b] li., light; ye., yellow; or., orange; bl., blue; gre., green; wh., white; pw., powder; cr., crystals; d., dark.

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

Compound	x-Sensitive *q*	x-Sensitive *r*	Out-of-plane ring deformation	x-Sensitive *y*
tpp	1089m		514s	
$[MBr_2(tpp)_2]$	1122m	726m	541s	
$[FeBr_2(tpp)_{1.5}]$	1121s	723s	541s	450w
$[CoBr_2(tpp)_2]$	1096s	707m	520s	
$[NiBr_2(tpp)_2]$	1095s	709m	519s	439w
$[CuBr(tpp)_3]$	1090s	705m	517s	425w
$[ZnBr_2(tpp)_2]$	1096s	707m	522s	

[a] Notation used is from Whiffen [15]. Intensity of bands: s, strong; m, medium; w, weak.

through the phosphorus atom [13–15]. Table 2 presents the more important IR bands of the adducts.

3.2. Thermal studies

Thermogravimetry and derivative thermogravimetry of the adducts showed that the thermal dissociation processes were of different types, with the lost of mass in 1 (Fe adduct), 2 (Ni adduct) or 3 (Mn, Co, Cu and Zn adducts) steps. Some of these steps consist of two successive decomposition processes (first step of Co, Ni or Cu adducts). They lose part of the ligand (or all in the case of Fe adduct) in the first step, following by loss of the rest of the ligand in the second step. Part or all the bromine is lost in the third step with the exception of the adduct of Fe that loses part of the bromine together with all the ligand in a unique step, the Mn adduct that loses bromine in the second and third steps and the Ni adduct that loses part of the bromine in the second step. The adducts also lose some or all metal in the third step with the exceptions of Fe and Ni adducts. In most cases a residue is observed, which is all or part of the respective metal [16].

The DSC curves of the adducts are consistent with the TG/DTG data and show endothermic peaks due to melting or elimination of part of the ligand. Table 3 presents 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. For the adduct of Mn(II), since only forbidden bands can be observed in the electronic spectra of high spin (II) compounds, it is impossible to determine with accuracy the ligand field parameters. It is, however, possible to deduce the local symmetry, which is pseudo-tetrahedral [17,18], with two phosphorus atoms from two ligand molecules and two bromide ions surrounding the

Table 3
Thermal analysis data of the compounds $[MBr_2(tpp)_n]$

Compound	Mass lost (%)		TG temperature range (K)	Species lost	DSC peak temperature	ΔH^{θ} ($kJ\,mol^{-1}$)
	Calculated	Observed				
$[MnBr_2(tpp)_2]$	60.31	59.43	443–497	−1.7 tpp	349	34.18
	14.96	15.73	497–681	−0.3 tpp −0.4 Br	439	9.34
	19.53	19.60	900–985	−1.6 Br −0.3 Mn		
		5.24[a]				
$[FeBr_2(tpp)_2]$	90.30	90.06	599–666	−2 tpp −1.8 Br	335	2.75
		9.94[a]			350	2.48
					415	10.57
$[CoBr_2(tpp)_2]$	52.92	53.85[b]	490–614	−1.5 tpp	440	0.44
	17.64	15.20	614–650	−0.5 tpp		
	24.28	25.75	650–870	−2 Br −0.35 Co		
$[NiBr_2(tpp)_2]$	67.07	67.01[b]	491–556	−1.9 tpp	337	23.19
	21.82	21.02	836–926	−0.1 tpp −1.7 Br		
		11.97[a]				
$[CuBr(tpp)_3]$	56.39	57.52[b]	451–553	−2 tpp	437	67.76
	28.20	27.06	553–602	−tpp	451	
	14.28	14.14	737–782	−Br −5/6 Cu		
$[ZnBr_2(tpp)_2]$	34.98	36.14	468–497	−tpp	326	6.85
	34.98	34.22	497–595	−tpp		
	30.04	31.75	597–746	−2 Br −Zn		

[a] Residue at 1233 K.

[b] Two overlapping steps.

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

Compound	Band maxima ($\times 10^3$ cm^{-1})	
	d-d	Intraligand + charge transfer
$[MnBr_2(tpp)_2]$	19.5, 21.4	36.3

	d-d		Intraligand + charge transfer
	ν_1[a]	Dq(cm^{-1})	
$[FeBr_2(tpp)_{1.5}]$	5.35	5352	20.7

	d-d		Intraligand + charge transfer	Dq (cm^{-1})	B (cm^{-1})	Dq/B	β^+
	ν_2	ν_3					
$[CoBr_2(tpp)_2]$	8.12[b]	14.9[c]	24.9	485	567	0.855	0.584
$[NiBr_2(tpp)_2]$	8.78[d]	16.9[e]	23.1	476	909	0.527	0.883

$\beta^+ = B/B_0$; $B_0 = 971$ cm^{-1}(Co^{2+}); $B_0 = 1030$ cm^{-1} (Ni^{2+}) [17].

[a] $\nu_1 = {}^5T_2 \leftarrow {}^5E$.

[b] $\nu_2 = {}^4T_1(F) \leftarrow {}^4A_2$.

[c] $\nu_3 = {}^4T_1(P)) \leftarrow {}^4A_2$.

[d] $\nu_2 = {}^3A_2 \leftarrow {}^3T_1(F)$.

[e] $\nu_3 = {}^3T_1 \leftarrow {}^3T_1(F)$.

Mn(II) ion. The ligand field parameters for the Fe(II) adduct were calculated according to Bolster et al. [17]. It is concluded by the position of the observed absorption band and considering the magnitude of Dq that the Fe(II) is pseudo-tetrahedrally surrounded by two phosphorus atoms from two ligand molecules and two bromide ions and another Fe(II) atom linking by a bromide bridge to the first Fe(II) atom, is pseudo-tetrtahedrally surrounded by one phosphorus atom from one ligand molecule and three bromide ions forming a dimeric structure. For the adduct of Co(II), the ligand field parameters were calculated according to Lever [19]. According to the number and position of the bands [17,20] and considering the magnitude of the crystal field parameters as compared with that of Bolster et al. [17], it is concluded that the adduct of Co(II) is pseudo-tetrahedrally surrounded by two phosphorus atoms from two ligand molecules and two bromide ions. The ligand field parameters for the Ni(II) adduct were calculated according to Reedijk et al. [21] and Lever [19]. According to the number and position of the observed bands and considering the magnitude of the crystal field parameters as compared with that of Brown et al. [18], it is concluded that the adduct of Ni(II) is pseudo-tetrahedrally surrounded by two phosphorus atoms from two ligand molecules and by two bromide ions.

3.4. Calorimetric measurements

The standard enthalpies of dissolution of metal(II) bromides, triphenylphosphine and adducts were obtained as previously reported [11]. The standard enthalpies of dissolution were obtained accordingly with the standard enthalpies of reactions (1)–(4) in solution:

$$MBr_{2(s)} + \text{calorimetric solvent} \rightarrow \text{solution A};\ \Delta_1 H^\theta \qquad (1)$$

$$n\,\text{tpp}_{(s)} + \text{solution A} \rightarrow \text{solution B};\ \Delta_2 H^\theta \qquad (2)$$

$$[MBr_2(tpp)_n]_{(s)} + \text{calorimetric solvent} \rightarrow \text{solution C};\ \Delta_3 H^\theta \qquad (3)$$

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

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 reaction (5):

$$MBr_{2(s)} + n\,\text{tpp}_{(s)} \rightarrow [MBr_2(tpp)_n]_{(s)};\ \Delta_r H^\theta = \Delta_1 H^\theta + \Delta_2 H^\theta - \Delta_3 H^\theta \qquad (5)$$

since the final state of reactions (2) and (3) is the same and $\Delta_4 H^\theta = 0$. Table 5 gives the values obtained for the enthalpies of dissolution of MBr_2 ($\Delta_1 H^\theta$), tpp into the solution of metal(II) bromide ($\Delta_2 H^\theta$) and of the adducts ($\Delta_3 H^\theta$). Unhappily, Cu(I) bromide and its adduct of tpp are extremely insoluble in most solvents and enthalpies of dissolution could not be determined. Uncertainty intervals given in Table 5 are twice the standard deviation of the means of 4–10 replicate measurements. Combined errors were calculated from the square root of the sum of the square of the component errors.

From the values obtained for the standard enthalpies of the acid/base reactions ($\Delta_r H^\theta$) and by using appropriate thermochemical cycles [11,22–24], the following thermochemical parameters for the adducts, 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 of the Lewis acid/base reactions in the gaseous phase ($\Delta_r H^\theta$(g)). These latter values can be used to calculate the standard enthalpies of the M–P bonds [22], being equal to: $\bar{D}_{(M-P)} = -\Delta_r H^\theta(g)/n$.

Table 5
Enthalpies of dissolution at 298.15 K

Compound	Calorimetric solvent	Number of experiments	(*i*)	$\Delta_i H^\theta$/kJ mol^{-1}
$MnBr_{2(s)}$	Methanol	6	1	−78.83 ± 1.36
$tpp_{(s)}$	2:1 MBr_2–Methanol	5	2	23.55 ± 1.09
$[MnBr_2(tpp)_2]_{(s)}$	Methanol	4	3	−29.70 ± 1.81
$FeBr_{2(s)}$	Methanol	5	1	−68.93 ± 0.76
$tpp_{(s)}$	1.5:1 $FeBr_2$–Methanol	5	2	20.92 ± 0.69
$[FeBr_2(tpp)_{1.5}]_{(s)}$	Methanol	4	3	35.08 ± 2.22
$CoBr_{2(s)}$	Methanol	4	1	−107.42 ± 3.37
$tpp_{(s)}$	2:1 $CoBr_2$–Methanol	4	2	20.10 ± 0.41
$[CoBr_2(tpp)_2]_{(s)}$	Methanol	4	3	22.50 ± 0.64
$NiBr_{2(s)}$	TEA–Methanol–CH_3CN[a]	4	1	−130.32 ± 4.30
$tpp_{(s)}$	2:1 TEA–Methanol–CH_3CN	4	2	23.98 ± 1.01
$[NiBr_2(tpp)_2]_{(s)}$	TEA–Methanol–CH_3CN	4	3	65.84 ± 1.95
$ZnBr_{2(s)}$	Methanol	10	1	−48.30 ± 0.64
$tpp_{(s)}$	2:1 $ZnBr_2$–Methanol	6	2	25.02 ± 1.17
$[ZnBr_2(tpp)_2]_{(s)}$	Methanol	4	3	63.01 ± 3.10

[a] 10% (v/v) triethanolamine, 40% (v/v) CH_3CN and 50% (v/v) methanol.

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

Compound	$\Delta_r H^\theta$	$\Delta_f H^\theta$	$\Delta_s^g H^\theta$	$\Delta_M H^\theta$	$\Delta_D H^\theta$	$\Delta_r H^\theta(g)$	$\bar{D}_{(M-O)}$
$MnBr_{2(s)}$		−384.9[a]	206[b]				
$FeBr_{2(s)}$		−249.8[a]	204[b]				
$CoBr_{2(s)}$		−220.9[a]	183[b]				
$NiBr_{2(s)}$		−212.1[a]	170[b]				
$ZnBr_{2(s)}$		−328.65[a]	159.7[b]				
$tpp_{(s)}$		218.0 ± 10.7[c]	96.2 ± 17.3[c]				
$[MnBr_2(tpp)_2]_{(s)}$	−25.58 ± 2.51	25.5 ± 21.6		−423.9 ± 34.7	218.0 ± 34.7	−327.7 ± 38.8	163.9 ± 19.4
$[FeBr_2(tpp)_{1.5}]_{(s)}$	−19.14 ± 2.09	167.1 ± 21.6		−416 ± 35	211.5 ± 34.7	−319 ± 39	213 ± 26
$[CoBr_2(tpp)_2]_{(s)}$	−109.82 ± 3.45	105.3 ± 21.8		−485 ± 35	302.2 ± 34.8	−389 ± 39	195 ± 20
$[NiBr_2(tpp)_2]_{(s)}$	−40.50 ± 4.83	183.4 ± 22.0		−403 ± 35	232.9 ± 34.9	−307 ± 39	154 ± 20
$[ZnBr_2(tpp)_2]_{(s)}$	−82.29 ± 3.37	21.1 ± 21.8		−438.4 ± 34.8	278.7 ± 34.8	−342.2 ± 38.9	171.1 ± 19.5

[a] [25].
[b] [26].
[c] [27].

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 enthalpies of sublimation of the adducts were equal to the enthalpy of sublimation of one mole of the ligand [28,29] as the melting points and/or thermal studies showed that the adducts decomposed on heating and were not found in the liquid state and probably not in the gaseous phase.

Based on $\Delta_r H^\theta$ values for the adducts, the acidity order of the salts can be obtained: $CoBr_2 > ZnBr_2 > NiBr_2 > MnBr_2$. Using the $\bar{D}_{(M-P)}$ values, the order is $CoBr_2 > ZnBr_2 > MnBr_2 > NiBr_2$.

The enthalpies for the process of hypothetical complex formation in the gaseous phase from metal(II) ions, bromide ions and tpp molecules, can be evaluated:

$$M_{(g)}{}^{2+} + 2Br_{(g)}{}^{-} + n\,tpp_{(g)} \rightarrow [MBr_2(tpp)_n]_{(g)};\ \Delta_{fI} H^\theta \tag{6}$$

where $\Delta_{fI} H^\theta = \Delta_f H^\theta(\text{adduct}_{(g)}) - \Delta_f H^\theta(M_{(g)}{}^{2+}) - 2\ \Delta_f H^\theta(Br_{(g)}{}^{-}) - n\ \Delta_f H^\theta(tpp_{(g)})$.

Table 7 lists the values obtained for these enthalpy values. Correlation of the $\Delta_{fI} H^\theta$ values with the metal atomic number for the adducts with stoichiometry 1:2 is presented in Fig. 1. The values obtained depend on the electronic structure of the central metallic ion. That relation allows determination of the thermodynamic stabilization energy in the ligand field on

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

Compound	$\Delta_f H^\theta$	$\Delta_r H^\theta(g)$	$\Delta_{fI} H^\theta$
$Br_{(g)}{}^{-}$	−219.07[a]		
$Mn_{(g)}{}^{2+}$	2522.0 ± 0.1[b]		
$Fe_{(g)}{}^{2+}$	2751.6 ± 2.3[b]		
$Co_{(g)}{}^{2+}$	2841.7 ± 3.4[b]		
$Ni_{(g)}{}^{2+}$	2930.5 ± 1.5[b]		
$Zn_{(g)}{}^{2+}$	2781.0 ± 0.4[b]		
$[MnBr_2(tpp)_2]_{(g)}$	122 ± 56	−327.7 ± 38.8	−2590 ± 69
$[FeBr_2(tpp)_{1.5}]_{(g)}$	263 ± 56	−319 ± 39	−2679 ± 69
$[CoBr_2(tpp)_2]_{(g)}$	201 ± 56	−389 ± 39	−2831 ± 69
$[NiBr_2(tpp)_2]_{(g)}$	279 ± 56	−307 ± 39	−2842 ± 69
$[ZnBr_2(tpp)_2]_{(g)}$	117.2 ± 56.2	−342.2 ± 38.9	−2854.1 ± 69.4

[a] [25].
[b] [30].

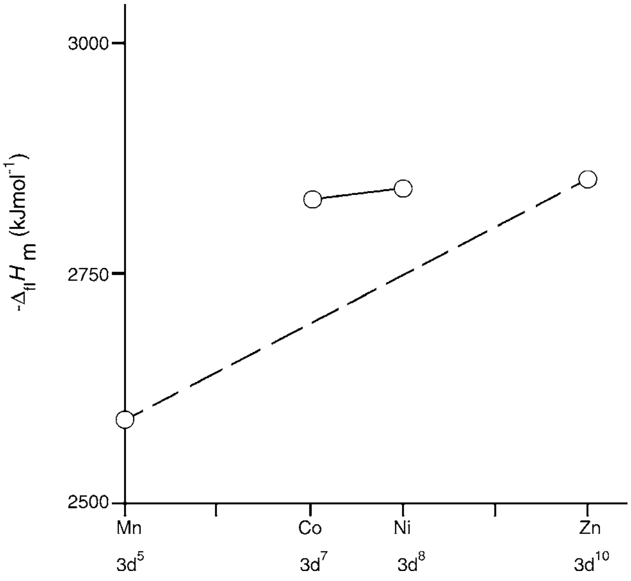

Fig. 1. Plot of the enthalpy change of complex formation in the gaseous phase from ionic components against d-electron configuration.

the assumption that variations of enthalpies of formation of the adducts in the gaseous phase is linear in a hypothetical state without influence of the ligand field. In such a case the stabilization energies are the difference between the real and the interpolated values. Thus, the stabilization energies in the ligand field formed by two bromide ions and two phosphorus atoms from two triphenyphosphine molecules increases in the order: Ni(II), 92 kJ/mol < Co(II), 136 kJ/mol.

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