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Thermochimica Acta 441 (2006) 1–7

thermochimica acta

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Review

Thermochemistry of adducts of some bivalent transition metal bromides with aniline

Pedro Oliver Dunstan [*]

Instituto de Química, Universidade Estadual de Campinas, C.P. 6154, CEP 13084-971, Campinas, São Paulo, Brazil

Received 15 July 2005; received in revised form 4 November 2005; accepted 15 November 2005

Abstract

The compounds $[MBr_2(an)_2]$ (where M is Mn(II), Fe(II), Co(II), Ni(II), Cu(II) or Zn(II); an = aniline) were synthesized and characterized by melting points, elemental analysis, thermal studies, and electronic and IR spectroscopy. The enthalpies of dissolution of the adducts, metal(II) bromides and aniline in methanol, aqueous 1.2 M HCl or 25% (v/v) aqueous 1.2 M HCl in methanol were measured. The following thermochemical parameters for the adducts have been determined by thermochemical cycles: the standard enthalpies for the Lewis acid/base reactions ($\Delta_r H^\circ$), the standard enthalpies of formation ($\Delta_f H^\circ$), the standard enthalpies of decomposition ($\Delta_D H^\circ$), the lattice standard enthalpies ($\Delta_M H^\circ$) and the standard enthalpies of the Lewis acid/base reactions in the gaseous phase ($\Delta_r H^\circ(g)$). The mean bond dissociation enthalpies of the M(II)–nitrogen bonds ($\bar{D}_{(M\text{–}N)}$) and the enthalpies of formation of the adducts from the ions in the gaseous phase: $M^{2+}{}_{(g)} + Br^-{}_{(g)} + an_{(g)} \rightarrow [MBr_2(an)_2]_{(g)}$, ($\Delta_{fi} H^\circ$) have been estimated.

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

Contents

1. Introduction

Thermochemical parameters related to transition metal–nitrogen coordinated bonds in coordination compounds formed by metal halides or pseudo-halides with aniline are not found in the literature. In earlier papers [1–10], the preparation and the spectroscopy in the UV, visible and IR spectra of these compounds are described. Also, dielectric measurements have been made on them [6].

The present paper is a calorimetric study of adducts of some divalent transition metal bromides and aniline, with the pur-

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[*] Tel.: +55 19 37883023; fax: +55 19 37883088.
E-mail address: dunstan@iqm.unicamp.br.

0040-6031/$ – see front matter
doi:10.1016/j.tca.2005.11.026

Table 1
Yields in %, appearance and analytical data on the compounds

Compound	Yield	mp[a] (K)	Appearance	C		H		N		Br		M	
				Calculated	Found	Calculated	Found	Calculated	Found	Calculated	Found	Calculated	Found
$[MnBr_2(an)_2]_n$	82	558	wh. pw.	35.94	35.87	3.52	3.47	6.99	6.94	39.85	39.75	13.70	13.65
$[FeBr_2(an)_2]_n$	8	448	l. br. pw.	35.86	35.75	3.51	3.63	6.97	6.89	39.76	39.70	13.89	13.85
$[CoBr_2(an)_2]$	27	532	l. bl. cr.	35.59	35.48	3.48	3.36	6.92	6.88	39.46	39.40	14.55	14.60
$[NiBr_2(an)_2]_n$	54	552	l. gre. cr.	35.61	35.48	3.49	3.56	6.92	6.81	39.48	39.47	14.50	14.49
$[CuBr_2(an)_2]$	73	443	d. br. pw.	35.19	35.16	3.45	3.32	6.84	6.80	39.02	39.00	15.51	15.43
$[ZnBr_2(an)_2]$	66	531	wh. cr.	35.03	35.08	3.43	3.40	6.81	6.81	38.84	38.85	15.89	15.90

l., light; d., dark; wh., white; br., brown; bl., blue; gre., green; pw. powder; cr., crystals.

[a] Melting with decomposition.

pose of determining the energy involved in the formation of the coordinated metal–nitrogen bonds and to determine several thermochemical parameters for the adducts. The knowledge of the thermodynamic properties of these compounds is important to help the understanding of the coordinated metal–nitrogen bonds, and to characterize and understand the properties of these coordination compounds, which eventually could be useful in determining their potential applications in catalysis or in the chromatographic separation of metal ions.

2. Experimental

2.1. Chemicals

Aniline (+99.5% Química Fina Ltd.) was purified by distillation through an efficient column. All the anhydrous metal(II) bromides used in the synthesis of the adducts were of reagent grade. Solvents used in the synthesis of the compounds and in the calorimetric measurements 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 contents were determined by complexometric titration with 0.01 M EDTA solution [11] of the aqueous solution of the adducts. Bromide analysis was obtained by gravimetry with standard 0.1 M $AgNO_3$ solution, after the adducts have been dissolved in water [12]. The capillary melting points of the adducts were determined in a UNIMELT equipment from Thomas Hover.

2.3. Adducts synthesis

The adducts were prepared by the reaction of the anhydrous metal(II) bromides dissolved in hot ethanol (acetone for Fe(II) bromide) with aniline. A typical procedure is given bellow.

To a solution of 1.5 g of $MnBr_2$ (6.98 mmol) in 40 mL of hot ethanol, 1.3 mL of aniline (13.96 mmol) was added, slowly and drop-wise with stirring. The white solid that formed was filtered and washed with tree portions of 10 mL of petroleum ether. The product was dried for several hours in vacuum and stored in a desiccator over calcium chloride. In all cases a molar ratio of salt/ligand of 1/2 was used.

2.4. Infrared spectra

Spectra were obtained with samples in KBr. For the liquid ligand, a film sandwiched between NaCl plates was used. A Perkin-Elmer 1600 series FT-IR spectrophotometer in the region 4000–400 cm^{-1} region was used.

2.5. Thermal studies

TG/DTG and DSC measurements were obtained in argon atmosphere in a Du Pont 951TG analyzer with the samples varying in mass from 3.02 to 6.84 mg (TG/DTG) and from 2.24 to 4.25 mg (DSC), and a heating rate of 10 K min^{-1} in the 293–513 K (DSC) and 298–1243 K (TG/DTG) temperature ranges. TG calibration for temperatures was made with metallic aluminum as a standard (mp = 660.37 °C). The equipment carried out the calibration for mass automatically. The DSC calibration was made with metallic indium as a standard (mp = 165.73 °C, $\Delta_s{}^{l}H^\circ = 28.4\ \mathrm{J\,g^{-1}}$).

2.6. Calorimetric measurements

All the solution calorimetric measurements were carried out in an LKB 8700-1 precision calorimeter as previously described [13]. The solution calorimetric measurements were performed by dissolving samples of 5.5–110.3 mg of the adducts or metal(II) bromides in 100 mL of methanol, aqueous 1.2 M HCl or 25% (v/v) aqueous 1.2 M HCl in methanol and the ligand aniline in this latter solution maintaining the molar relation of 1/2, equal to the stoichiometry of the adduct. The accuracy of the calorimeter was verified by determining the heat of dissolution of tris[(hydroxymethyl)amino]methane in 0.1 mol dm^{-3} HCl. The result 29.78 ± 0.03 k J mol^{-1}, is in agreement with the value recommended by IUPAC (-29.763 ± 0.003 kJ mol^{-1}) [14].

2.7. Electronic spectra

Spectra in the 350–2000 nm region were obtained with a UV–vis–NIR Varian-Cary 5G spectrophotometer, with a standard reflectance attachment for obtaining the spectra of the solid adducts.

Table 2
Infrared data[a] for aniline and complexes

Compound	N–H$_{\text{stretching}}$ (cm^{-1})	N–H$_{\text{deformation}}$ (cm^{-1})
an	3433 s, 3355 s	1617 s
$[MnBr_2(an)_2]$	3302 m, 3241 m	1607 m
$[FeBr_2(an)_2]$	3384 m, b, 2859 m, b	1600 m
$[NiBr_2(an)_2]$	3361 m, 3315 m	1603 s
$[CoBr_2(an)_2]$	3257 m, 3211 m	1604 s
$[CuBr_2(an)_2]$	3296 m, 3230 m	1601 m
$[ZnBr_2(an)_2]$	3263 m, 3219 m	1604 m

[a] Intensity of bands: s, strong; m, medium; b, broad.

3. Results and discussion

All adducts obtained were solids. The yields ranged from 27 to 82%. The yields, melting points, colors, appearance and analytical data are summarized in Table 1. All of the compounds melted with decomposition.

3.1. Infrared spectra

The infrared spectra of the adducts is similar to that of free aniline. There is a shift of the N–H stretching and bending modes of the adducts to lower frequencies, indicating a weakening of this bond after coordination of the nitrogen atom to the metal ion [10, 15–21]. Table 2 presents the extracted infrared spectral data for N–H stretching and bending frequencies of adducts and ligand.

3.2. Thermal studies

Thermogravimetry and derivative thermogravimetry of the adducts showed that the associated thermal dissociation process were of different types, with the lost of mass in three steps. Some of these steps consist of two successive decomposition processes. They lose part of the ligand in the first two steps (Cu adduct), or all the ligand and part of the bromine (Mn, Fe and Ni adducts) or all the ligand, all the bromine and part of the metal (Zn adduct). In the third step, the adducts of Mn, Co and Ni lose part of the bromine. The adduct of Fe lost the rest of the bromine and part of the metal in the third step. The adduct of Cu lose the rest of the ligand, all the bromine and part of the metal in the third step. The adduct of Zn lost part of the metal in the third step. In all cases a residue is observed that is part of the metal or a mixture of metal and metal bromide. For the heating of metal(II) bromides the loss of all the bromide and part of the metal or part of the bromine has been observed, leading to a residue of the respective metal or a mixture of the metal and metal bromide [22].

The DSC curves of the adducts are consistent with the TG/DTG data and show endothermic peaks due to melting with the partial elimination of the ligand, partial elimination of ligand and or partial elimination of the ligand together with the partial elimination of bromine. Table 3 presents the thermoanalytical data on the adducts.

Table 3
Thermal analysis of the compounds

Compound	Mass lost (%)		TG temperature range (K)	Species lost	DSC peak temperature	ΔH° (kJ mol^{-1})
	Calculated	Observed				
$[MnBr_2(an)_2]$	6.97	7.8	331–342	−0.3 L	368	57.83
	41.48	41.48	416–450	−0.7 L–0.1 Br		
	36.86	36.19	858–976	−1.85 Br		
		15.25[a]				
$[FeBr_2(an)_2]$	48.33	48.35	421–477	−2 L–0.1 Br	449	98.51
	9.96	10.80	477–574	− 0.5 Br		
	29.21	29.21	590–787	−1.4 Br–0.1 Fe		
		11.44[a]				
$[CoBr_2(an)_2]$	43.70	44.20	451–487	−1.9 L	307	0.37
	37.81	37.74	827–931	−0.1 L–1.8 Br	330	0.56
	0.58	0.62	1067–1102	−0.03 Br	452	0.06
		17.44[a]				
$[NiBr_2(an)_2]$	17.26	17.73	360–328	−0.75 L	335	9.68
	36.66	36.53	328–484	−1.25 L–0.4 Br	397	96.78
	29.61	29.95	820–918	−1.5 Br		
		15.79[a]				
$[CuBr_2(an)_2]$	12.51	12.40	369–389	−0.55 L	370	23.14
	14.78	14.80	389–552	−0.65 L	423	12.40
	61.09	61.24	389–961	−0.8 L–2 Br–0.25 Cu		
		11.56[a]				
$[ZnBr_2(an)_2]$	33.95	33.97	455–497	−1.5 L	335	20.01
	58.89	58.73	497–724	−0.5 L–2 Br–0.55 Zn		
	2.38	2.30	724–908	−0.15 Zn		
		5.00[a]				

[a] Residue at 1243 K.

3.3. Electronic spectra

The ligand field parameters for the Co(II) adduct were calculated according to Lever [23]. According to the number and position of the bands [24,25] and considering the magnitude of the crystal field parameters as compared with that of Bolster [26], it is concluded that the Co(II) ion is pseudo-tetrahedrally surrounded [8] by two nitrogen atoms from two ligand molecules and by two bromide ions. The ligand field parameters for the NI(II) adduct were calculated according to Reedijk et al. [27] and Lever [23]. According to the number and position of the observed bands, and considering the magnitude of the crystal field parameters as compared with that of Bolster [26], it is concluded that the Ni(II) ion is pseudo-octahedrally [8] surrounded by two nitrogen atoms from two ligand molecules and by four bromide ions. For the adduct of Mn(II) since only spin-forbidden bands can be observed in the electronic spectra of high-spin(II) complexes, it is impossible to determine with accuracy the ligand field parameters. It is however, possible to deduce the local symmetry, which is pseudo-octahedral [8,24,26] with two nitrogen atoms from two ligand molecules and four bromide ions surrounding the Mn(II) ion. The ligand field parameters for the Fe(II) adduct were calculated according to Bolster [26]. It is concluded by the position of the absorption band and considering the magnitude of Dq that the Fe(II) is pseudo-tetrahedrally surrounded by two nitrogen atoms from two ligand molecules and by two bromide ions. For the Cu(II) adduct, the electronic spectrum showed a rather broad band with two maxima. The intensity and position correspond with those observed in pseudo-tetrahedral Cu(II) compounds [26,28], the Cu(II) ion being surrounded by two nitrogen atoms from two ligand molecules and by two bromide ions. Table 4 contains the band maxima assignments and calculated ligand field parameters for the adducts.

3.4. Calorimetric measurements

The standard enthalpies of dissolution of metal(II) bromides, aniline and adducts were obtained as previously reported [13]. The standard enthalpies of dissolution were obtained according to the standard enthalpies of the following reactions in solution:

$$\mathrm{MBr_{2(s)}} + \text{calorimetric solvent} \rightarrow \text{solution A}, \quad \Delta_1 H^\circ \tag{1}$$

$$2\mathrm{an_{(l)}} + \text{solution A} \rightarrow \text{solution B}, \quad \Delta_2 H^\circ \tag{2}$$

$$[\mathrm{MBr_2(an)_2}]_{(s)} + \text{calorimetric solvent} \rightarrow \text{solution C}, \quad \Delta_3 H^\circ \tag{3}$$

$$\text{Solution B} \rightarrow \text{solution C}, \quad \Delta_4 H^\circ \tag{4}$$

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

$$\mathrm{MBr_{2(s)}} + 2\mathrm{an_{(l)}} \rightarrow [\mathrm{MBr_2(an)_2}]_{(s)}, \quad \Delta_r H^\circ \tag{5}$$

where $\Delta_r H^\circ = \Delta_1 H^\circ + \Delta_2 H^\circ - \Delta_3 H^\circ$

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

Compound	Band maxima ($\times 10^3$ cm^{-1})	
	d–d	Intra-ligand + charge transfer
$[\mathrm{MnBr_2(an)_2}]_n$	18.5, 23.5	28.4, 29.2
$[\mathrm{CuBr_2(an)_2}]$	10.5, 12.4	

	Band maxima ($\times 10^3$ cm^{-1})		
	d–d		Intra-ligand + charge transfer
	ν_1	Dq (cm^{-1})	
$[\mathrm{FeBr_2(an)_2}]_n$	12.38[a]	1238	28.0

	Band maxima ($\times 10^3$ cm^{-1})					Dq (cm^{-1})	B (cm^{-1})	Dq/B	β^+
	d–d				Intra-ligand + charge transfer				
	ν_1	ν_2	ν_4	ν_3					
$[\mathrm{CoBr_2(an)_2}]$		7.07[b]		15.9[c]	28.4	275	983	0.28	1.01
$[\mathrm{NiBr_2(an)_2}]_n$	8.34[d]	12.9[e]	14.1[f]	23.8[g]	27.5, 28.6	834	535	1.56	0.52

$\beta^+ = B/B_0$; $B_0 = 971$ cm^{-1} (Co^{2+}); $B_0 = 1030$ cm^{-1} (Ni^{2+}); reference [26].

[a] $\nu_1 = {}^5E_g \leftarrow {}^5T_{2g}$.

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

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

[d] $\nu_1 = {}^3T_{2g} \leftarrow {}^3A_{2g}$.

[e] $\nu_2 = {}^3T_{1g}(F) \leftarrow {}^3A_{2g}$.

[f] $\nu_4 = {}^1E_g \leftarrow {}^3A_{2g}$.

[g] $\nu_3 = {}^3T_{1g}(P) \leftarrow {}^3A_{2g}$.

Table 5
Enthalpies of dissolution at 298.15 K

Compound	Calorimetric solvent[a]	Number of experiments	i	$\Delta_i H^\circ$ (kJ mol^{-1})
$MnBr_{2(s)}$	Methanol	9	1	−76.58 ± 1.78
$an_{(l)}$	2:1 MBr_2–methanol	4	2	−4.62 ± 0.10
$[MnBr_2(an)_2]_{(s)}$	Methanol	4	3	−17.97 ± 0.90
$FeBr_{2(s)}$	Methanol	7	1	−79.21 ± 2.10
$an_{(l)}$	2:1 $FeBr_2$–methanol	6	2	−11.42 ± 0.45
$[FeBr_2(an)_2]_{(s)}$	Methanol	4	3	25.63 ± 1.14
$CoBr_{2(s)}$	Methanol	9	1	−105.99 ± 1.22
$an_{(l)}$	2:1 $CoBr_2$–methanol	4	2	−4.73 ± 0.15
$[CoBr_2(an)_2]_{(s)}$	Methanol	4	3	−13.16 ± 0.36
$NiBr_{2(s)}$	1.2 M HCl[a]	9	1	−58.75 ± 1.05
$an_{(l)}$	2:1 $NiBr_2$–1.2 M HCl[a]	4	2	−58.88 ± 1.53
$[NiBr_2(an)_2]_{(s)}$	1.2 M HCl[a]	4	3	−24.18 ± 1.16
$CuBr_{2(s)}$	25% 1.2 M HCl–methanol[b]	5	1	−25.41 ± 0.23
$an_{(l)}$	2:1 $CuBr_2$–25% 1.2 M HCl–methanol[b]	5	2	−45.62 ± 0.88
$[CuBr_2(an)_2]_{(s)}$	25% 1.2 M HCl–methanol[b]	5	3	9.30 ± 0.50
$ZnBr_{2(s)}$	Methanol	12	1	−48.39 ± 0.54
$an_{(l)}$	2:1 $ZnBr_2$–methanol	4	2	−4.93 ± 0.09
$[ZnBr_2(an)_2]_{(s)}$	Methanol	4	3	43.90 ± 0.49

[a] 1.2 M HCL = aqueous 1.2 M HCl.
[b] 25% 1.2 M HCl–methanol = 25% (v/v) aqueous 1.2 M HCl in methanol.

Since the final thermodynamic state of reactions (2) and (3) is the same and $\Delta_4 H^\circ = 0$. Table 5 gives the values obtained for the enthalpies of dissolution of MBr_2 ($\Delta_1 H^\circ$), aniline into the solution of MBr_2 ($\Delta_2 H^\circ$) and of the adducts ($\Delta_3 H^\circ$). Uncertainty intervals given in this table are twice the standard deviation of the means of 4–12 replicate measurements. Electronic spectra revealed that the adducts of Mn(II), Fe(II) and Ni(II) in the solid state are polymeric structures with chains formed by bridges of bromide ions linking the metallic ions [8]. The thermochemical parameters were calculated for monomeric hypothetical adducts of Mn(II), Fe(II) and Ni(II) adducts in the solid phase. From the values obtained for the standard acid/base reactions ($\Delta_r H^\circ$) and by using appropriate thermochemical cycles [13,29,30], the following thermochemical parameters for the adducts were determined: the standard enthalpies of formation ($\Delta_f H^\circ$), the standard enthalpies of decomposition ($\Delta_D H^\circ$), the standard lattice enthalpies ($\Delta_M H^\circ$) and the standard enthalpies of the Lewis acid/base reactions in the gaseous phase ($\Delta_r H^\circ(g)$). These latter values can be used to calculate the standard enthalpies of the M–N bonds [30], being equal to $\bar{D}_{(M-N)} = -\Delta_r H^\circ(g)/2$. Table 6 lists the values obtained for all these thermochemical parameters. Combined errors showed in this table were calculated from the square root of the sum of the component errors.

For the determination of $\Delta_r H^\circ(g)$ it was necessary to assume that the molar standard enthalpies of sublimation of the adducts were equal to the enthalpy of vaporization of one mol of the ligand [30,34] as the melting points and/or thermal studies showed that the adducts decomposed on heating and were not found in the liquid phase, and probably not in the gaseous phase.

Based on the $\Delta_r H^\circ$ values for the adducts, the acidity order of the salts can be obtained: $FeBr_2 > CoBr_2 \cong ZnBr_2 >$

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

Compound	$\Delta_r H^\circ$	$\Delta_f H^\circ$	$\Delta_s^g H^\circ$	$\Delta_M H^\circ$	$\Delta_D H^\circ$	$\Delta_r H^\circ(g)$	$\bar{D}_{(M-N)}$
$MnBr_{2(s)}$		−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]				
$CuBr_{2(s)}$		−141.8[a]	182.4[b]				
$ZnBr_{2(s)}$		−328.65[a]	159.7[b]				
$an_{(l)}$		31.3 ± 0.7[c]	55.8 ± 1.1[c]				
$[MnBr_2(an)_2]_{(s)}$	−63.23 ± 2.00	−384.5 ± 3.2		−379.7 ± 3.6	49.4 ± 3.0	−324.9 ± 3.7	162.5 ± 1.9
$[FeBr_2(an)_2]_{(s)}$	−116.26 ± 2.43	−303.5 ± 3.4		−432 ± 4	227.9 ± 3.3	−376 ± 4	188 ± 2
$[CoBr_2(an)_2]_{(s)}$	−97.56 ± 1.28	−255.9 ± 2.8		−392 ± 3	209.2 ± 2.5	−336 ± 3	168 ± 2
$[NiBr_2(an)_2]_{(s)}$	−93.45 ± 2.19	−243.0 ± 2.8		−375 ± 4	18.2 ± 3.1	−319 ± 4	160 ± 2
$[CuBr_2(an)_2]_{(s)}$	−80.33 ± 1.04	−238.6 ± 2.6		−374.3 ± 3.1	31.3 ± 2.4	−318.5 ± 3.3	159.3 ± 1.7
$[ZnBr_2(an)_2]_{(s)}$	−97.22 ± 0.73	−363.3 ± 2.5		−49.1 ± 3.1	208.8 ± 2.3	−312.7 ± 3.3	156.4 ± 1.7

[a] See reference [31].
[b] See reference [32].
[c] See reference [33].

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

Compound	$\Delta_f H^\circ$	$\Delta_r H^\circ$	$\Delta_{fI} H^\circ$
$Br^-_{(g)}$	-219.07[a]		
$Mn^{2+}_{(g)}$	2522.0 ± 0.1[b]		
$Fe^{2+}_{(g)}$	2751.6 ± 2.3[b]		
$Co^{2+}_{(g)}$	2841.7 ± 3.4[b]		
$Ni^{2+}_{(g)}$	2930.5 ± 1.5[b]		
$Cu^{2+}_{(g)}$	3054.5 ± 2.1[b]		
$Zn^{2+}_{(g)}$	2781.0 ± 0.4[b]		
$[MnBr_2(an)_2]_{(g)}$	-330 ± 5	-324.9 ± 3.7	-2588 ± 6
$[FeBr_2(an)_2]_{(g)}$	-248 ± 5	-376 ± 4	-2736 ± 6
$[CoBr_2(an)_2]_{(g)}$	-200 ± 4	-336 ± 3	-2778 ± 6
$[NiBr_2(an)_2]_{(g)}$	-187 ± 5	-319 ± 4	-2854 ± 6
$[CuBr_2(an)_2]_{(g)}$	-103.7 ± 4.4	-318.5 ± 3.3	-2894.3 ± 5.7
$[ZnBr_2(an)_2]_{(g)}$	-307.5 ± 4.1	-312.7 ± 3.3	-2824.6 ± 5.1

[a] See reference [31].

[b] See reference [32].

$NiBr_2 > CuBr_2 > MnBr_2$. Using the $\bar{D}_{(M–N)}$ values, the order is: $FeBr_2 > CoBr_2 > MnBr_2 > NiBr_2 > CuBr_2 > ZnBr_2$.

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

$$M^{2+}{}_{(g)} + 2Br^-{}_{(g)} + 2an_{(g)} \rightarrow [MBr_2(an)_2]_{(g)}, \quad \Delta_{fI} H^\circ \qquad (6)$$

with $\Delta_{fI}H^\circ = \Delta_f H^\circ(\text{adduct}_{(g)}) - \Delta_f H^\circ(M^{2+}{}_{(g)}) - 2\Delta_f H^\circ(Br^-{}_{(g)}) - 2\Delta_f H^\circ(an_{(g)})$.

Table 7 lists the values obtained for these enthalpy values. The environment around the M(II) ions is pseudo-tetrahedral (two Br ions and two N atoms). The correlation of the $\Delta_{fI}H^\circ$ values with the metal atomic number is presented in Fig. 1. It shows part of the double periodic variation profile. The $\Delta_{fI}H^\circ$ values obtained depends on the electronic structure of the central ion. The course of that relation allows determining graphically the thermodynamic stabilization energy in the ligand field, on the assumption that the course of the variation of the enthalpy values is linear in a hypothetical state without the influence of the ligand field. The stabilization energies are the difference between the real and the interpolated values. Thus, it is found that the stabilization energies in the ligand field formed by two bromide ions and two nitrogen atoms (from two ligand molecules) decreases in the order: Ni(II) 125 kJ mol^{-1} > Cu(II) 110 kJ mol^{-1} > Fe(II) 100 kJ mol^{-1} > Co(II) 90 kJ mol^{-1}. The adducts of Cu(II) bromide, of the same stoichiometry, formed with pyNO [32], α-picoNO [35] and β-picoNO [36] have stabilization energies of 107.5, 115 and 129 kJ mol^{-1}, respectively. This means that the order of stabilization energies of the ligands is: pyNO < an < α-picoNO < β-picoNO.

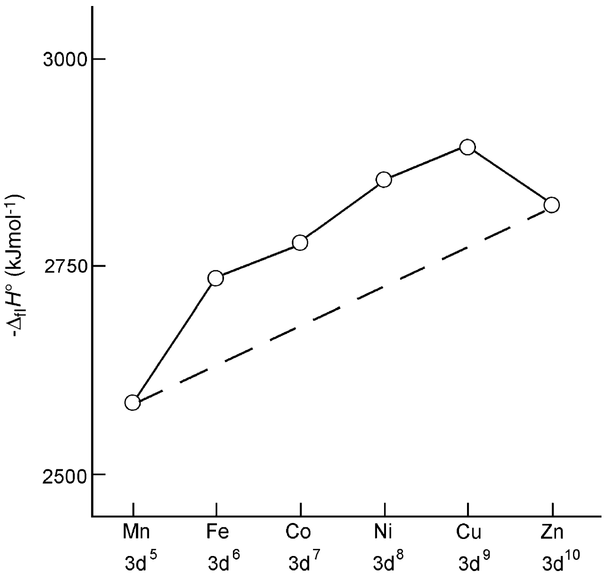

Fig. 1. Plot of the enthalpy change of complex formation in the gaseous phase from ionic components against d-electron configuration.

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