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Thermochemistry of adducts of some bivalent transition metal bromides with 4-chloroaniline

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Abstract

The compounds [$MBr_2(p\text{-clan})_2$] (where M is Mn(II), Fe(II), Co(II), Ni(II), Cu(II) or Zn(II); *p*-clan = 4-chloroaniline) were synthesized and characterized by melting points, elemental analysis, thermal analysis and electronic and IR spectroscopy. The enthalpies of solution of the adducts, metal(II) bromides and 4-chloroaniline in methanol, 1.2 M aqueous HCl or 25% (v/v) 1.2 M aqueous HCl in methanol were measures and by using thermochemical cycles, the following thermochemical parameters for the adducts have been determined: 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 metal(II)-nitrogen coordinated bonds ($\bar{D}_{(M-N)}$) and the enthalpies of adduct formation in the gaseous phase have been estimated.

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

1. Introduction

Thermochemical parameters related to transition metal–nitrogen coordinated bonds in coordination compounds formed by metal(II) halides with aniline derivatives are not found in the literature. In earlier papers [1–10], the preparations of metal(II) halides and pseudo-halides complexes of aniline and derivatives have been reported. Their spectrochemistry is discussed on the basis of UV, visible and IR spectra. Also, dielectric measurements have been made on them [6].

In a previous article [11], it is reported the calorimetric study of metal(II) bromides complexes of aniline. The present article is a calorimetric study of the complexes formed by some metal(II) bromides with 4-chloroaniline to determine the energy of the coordinated metal–nitrogen bonds formed in these compounds. The substitution of one hydrogen atom in the phenyl group of the aniline molecule by the electron-withdrawing chlorine atom is expected to cause a decrease in the electronic density of the aromatic ring. Consequently, by an inductive effect, the electronic density on the nitrogen atom will also be decreased and the energy of the coordinated metal(II)–nitrogen bond would be affected.

The knowledge of the thermodynamic properties of this kind of compounds is important to help in the understanding of the coordinated bonds formed, as well as, to characterize and understand the complexes properties.

2. Experimental

2.1. Chemicals

4-Chloroaniline (99%, BDH Limited Poole England) was purified by recrystallization from ethanol. All the anhydrous metal(II) bromides used in the preparation of the adducts were of the 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

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[12] of the aqueous solution of the adduct samples. Bromine analysis was obtained by gravimetry using standard 0.1 M aqueous $AgNO_3$ solution, after the adducts had been dissolved in water [13]. The capillary melting points of the adducts were determined by using a UNIMELT equipment from Thomas Hover.

2.3. Adducts synthesis

The adducts were prepared by the reaction of the hot solution in ethanol (Mn(II), Co(II) or Ni(II)) or in acetone (Fe(II), Cu(II) or Zn(II)) of the anhydrous metal(II) bromides with the hot solution of 4-chloroaniline in the same solvent. In all cases it was used a molar ratio salt/ligand of 1/2. *n*-Hexane was used for washing the obtained compounds. A typical procedure is given below.

To a solution of 1.5 g of $MnBr_2$ (6.98 mmol) in 40 mL of hot ethanol, 1.78 g of *p*-clan (13.97 mmol) in 20 mL of hot ethanol was slowly added drop-wise under stirring. The slightly pink solid that formed was filtered and washed with three portions of 20 mL of *n*-hexane. The product was dried for several hours in vacuum and 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 FT-IR spectrophotometer in the 4000–400 cm^{-1} region was used. Spectra in the 400–100 cm^{-1} region was obtained by using a Bomem FT DA8 spectrophotometer, with sample mulls of the adducts in Nujol sandwiched between polyethylene plates.

2.5. Thermal studies

The TG/DTG and DSC measurements were obtained in argon atmosphere in a Du Pont 951TG analyzer with the samples varying in mass from 4.60 to 8.11 mg (TG/DTG) and from 2.55 to 6.54 mg (DSC) and a heating rate of 10 K min^{-1} in the 298–573 K (DSC) and 298–1250 K (TG/DTG) temperature ranges. TG calibration for temperatures was made using metallic aluminum as a standard (mp = 660.37 °C) and the equipment carried out the calibration for mass automatically. The DSC calibration was made by using metallic indium as a standard (mp = 165.73 °C, $\Delta_{1s}H^\circ = 28.4\ J\ g^{-1}$).

2.6. Calorimetric measurements

All the solution calorimetric measurements were carried out in an LKB 8700-1 precision calorimeter as described before [14]. The solution calorimetric measurements were performed by dissolving samples of 4.2–81.7 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 4-chloroaniline 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 $-29.78 \pm 0.03\ kJ\ mol^{-1}$ is in agreement with the value recommended by IUPAC ($-29.763 \pm 0.003\ kJ\ mol^{-1}$) [15].

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.

3. Results and discussion

All the adducts were obtained in the solid state. The yields range from 19 to 78%. The yields, melting points, colors, appearance and analytical data are summarized in the Table 1.

3.1. Infrared spectra

The infrared spectra of 4-chloroaniline adducts show dislocation of some bands when compared with the spectrum of the free ligand. The pattern of the spectra of the adducts is similar to that of the free ligand. There are shifts of the N–H stretching and bending modes of the adducts to lower frequencies when compared with the free ligand, indicating a weakening of this bond after coordination of the nitrogen atom of the ligand to the metallic ion [10,16–23]. Table 2 presents the extracted infrared spectral data for N–H stretching and bending frequencies of

Table 1
Yields in %, melting points, appearance and analytical data of the compounds

Compound	Yield	mp (K)[a]	Appearance	C		H		N		Br		M	
				Calculated	Found	Calculated	Found	Calculated	Found	Calculated	Found	Calculated	Found
[$MnBr_2$(*p*-clan)$_2$]	43	531	wh., pw.	30.67	30.45	2.57	2.65	5.96	5.89	34.01	33.97	11.69	11.53
[$FeBr_2$(*p*-clan)$_2$]	46	376	l., br., pw.	30.61	30.63	2.57	2.67	5.95	5.72	33.95	33.80	11.86	11.77
[$CoBr_2$(*p*-clan)$_2$]	19	511	l., bl., cr.	30.42	30.59	2.55	2.53	5.91	5.85	33.72	33.54	12.43	12.36
[$NiBr_2$(*p*-clan)$_2$]	49	593	l., gr., cr.	30.43	30.31	2.55	2.65	5.91	5.86	33.74	33.56	12.39	12.19
[$CuBr_2$(*p*-clan)$_2$]	62	370	d., br., pw.	30.12	30.01	2.53	2.48	5.85	5.75	33.40	33.48	13.28	13.06
[$ZnBr_2$(*p*-clan)$_2$]	78	496	wh., cr.	30.01	29.95	2.52	2.48	5.83	5.69	33.27	33.16	13.61	13.58

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

[a] Melting with decomposition.

Table 2
IR spectral data[a]

Compound	N–H$_{\text{stretching}}$ (cm^{-1})	N–H$_{\text{deformation}}$ (cm^{-1})	M–N$_{\text{stretching}}$ (cm^{-1})	M–Br$_{\text{stretching}}$ (cm^{-1})
p-clan	3472m, 3382m	1617s		
[MnBr$_2$(p-clan)$_2$]	3383s	1617s	401m, 388m	251m, 172s
[FeBr$_2$(p-clan)$_2$]	3439m, 2861m	1610m	410m, 383m	286s, 184s
[CoBr$_2$(p-clan)$_2$]	3412m, 3228m	1574m	425s, 390s	250s, 208s
[NiBr$_2$(p-clan)$_2$]	3454s, 3314s	1603m	393m, 379m	221m, 167s
[CuBr$_2$(p-clan)$_2$]	3419m, 3293m	1561m	378s	267m, 218s
[ZnBr$_2$(p-clan)$_2$]	3386m, 3217m	1600m	426s, 385s	264m, 231s

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

the adducts and ligand. The metal–nitrogen stretching modes are assigned in the low frequency IR region, at 426–378 cm^{-1} [24,25] for all the adducts. These are also presented in Table 2.

3.2. Thermal studies

Thermogravimetry and derivative thermogravimetry of the adducts showed that the associated thermal dissociation processes were of different types with the lost of mass in two or three steps. Some of these steps consist of two or three successive decomposition processes. They loss all the ligand in the first two steps (three steps for the Cu(II) adduct). The adduct of Mn(II) losses part of the bromine content in the third step. The adducts of Fe(II), Co(II) and Ni(II) loss all the bromine in the third step and the adduct of Zn(II) losses all the bromine in the second step. The adducts of Fe(II) and Cu(II) also loss part of the metal content in the third step. It is observed a residue in all cases, which is the respective metal or part of it. In the cases of Mn(II) and Co(II) adducts, these residues are a mixture of the metal content with part of the bromine content [26].

The DSC curves of the adducts are consistent with the TG/DTG data and show endothermic peaks due to partial elimination of ligand and exothermic peaks due to decomposition with elimination of bromine. 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. The ligand field parameters for the Co(II) adduct were calculated according to Lever [28]. According to the number and position of the bands [29,30] and considering the magnitude of the crystal field param-

Table 3
Thermal analysis data of the compounds

Compound	Mass lost (%)		TG temperature range (K)	Species lost	DSC peak temperature (K)	ΔH° (kJ mol^{-1})
	Calculated	Observed				
[MnBr$_2$(p-clan)$_2$]	53.25	54.29	323–462	−2 L	359	29.59
	31.54	31.53	846–1009	−1.85 Br	400	1.05
		15.22[a]				
[FeBr$_2$(p-clan)$_2$]	29.81	30.19	376–419	−1.1 L	350	7.71
	29.48	29.41	419–488	−0.9 L–0.3 Br	382	14.87
	31.23	31.47	488–862	−1.7 Br–0.2 Fe	412	−98.40
		8.93[a]				
[CoBr$_2$(p-clan)$_2$]	51.15	51.59	454–486	−1.9 L	472	3.71
	34.73	34.85	846–1047	−0.1 L–1.9 Br		
		13.56[a]				
[NiBr$_2$(p-clan)$_2$]	8.08	7.82	356–378	−0.3 L	387	59.64
	48.31	48.55	378–498	−1.7 L–0.15 Br	408	5.87
	31.21	31.49	833–929	−1.85 Br		
		12.14[a]				
[CuBr$_2$(p-clan)$_2$]	23.99	24.12	361–427	−0.9 L	368	−35.88
	13.33	13.27	427–734	−0.5 L	416	−20.05
	60.68	60.67	734–1079	−0.6 L–2 Br–0.85 Cu	464	−13.33
		1.94[a]				
[ZnBr$_2$(p-clan)$_2$]	39.84	39.06	455–500	−1.5 L	510	−82.81
	54.04	54.80	500–735	−0.5 L–2 Br–0.55 Zn		
	4.62	4.62	735–1033	−0.34 Zn		
		1.52[a]				

[a] Residue at 1243 K.

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
[$MnBr_2$(p-clan)$_2$]	18.5, 23.3	31.3, 35.3

Compound	Band maxima ($\times 10^3$ cm^{-1})		
	d–d		Intraligand + charge transfer
	ν_1	Dq (cm^{-1})	
[$FeBr_2$(p-clan)$_2$]	12.25[a]	1225	22.3, 36.0

Compound	Band maxima ($\times 10^3$ cm^{-1})								
	d–d								Intraligand + charge transfer
	ν_1	ν_2	ν_4	ν_3	Dq (cm^{-1})	B (cm^{-1})	Dq/B	β^+	
[$CoBr_2$(p-clan)$_2$]		6.69[b]		15.9[c]	386	737	0.52	0.76	27.6, 32.9
[$NiBr_2$(p-clan)$_2$]	8.32[d]	12.4[e]	14.3[f]	23.8[g]	832	443	1.88	0.43	27.5, 28.6

Compound	Band máxima ($\times 10^3$ cm^{-1}), (d-d)
[$CuBr_2$(p-clan)$_2$]	10.6, 12.5

$\beta^+ = B/B_0$; $B_0 = 971$ cm^{-1} (Co^{2+}); $B_0 = 1030$ cm^{-1} (Ni^{2+}) [27].

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

eters as compared with that of Bolster [27], it is concluded that the adduct of Co(II) is pseudo-tetrahedrally surrounded by two nitrogen atoms from two ligand molecules and by two bromide ions. The ligand field parameters for Ni(II) adduct were calculated according to Reedijk et al. [31] and Lever [28]. According to the number and positions of the observed bands and considering the magnitude of the crystal field parameters as compared with that of Bolster [27], it is concluded that the adduct of Ni(II) is pseudo-octahedrally surrounded by two nitrogen atoms from two ligand molecules and by four bromide ions in a bridging polymeric structure [8]. The ligand field parameters for the Fe(II) adduct were calculated according to Bolster [27]. 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 adduct of Mn(II) since only spin-forbidden bands can be observed in the electronic spectra of high-spin (II) compounds, it is impossible to determined wit accuracy the ligand field parameters. It is however, possible to deduce the local symmetry which is pseudo-octahedral [8,29,30] with two nitrogen atoms from two ligand molecules and four bromide ions surrounding the Mn(II) ion in a bridge structure. For the Cu(II) adduct, the electronic spectra show a rather broad band with two maximums. Its intensity and positions correspond with those observed in pseudo-tetrahedral Cu(II) compounds [24,27], the Cu(II) ion being surrounded by two nitrogen atoms from two ligand molecules and by two bromide ions.

3.4. Calorimetric measurements

The standard enthalpies of dissolution of metal(II) bromides, p-chloroaniline and adducts were obtained as previously reported [14]. The standard enthalpies of dissolution were obtained according to the standard enthalpies of the following reactions in solution:

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

$$2p\text{-clan}_{(s)} + \text{solution A} \rightarrow \text{solution B}, \qquad \Delta_2 H^\circ \quad (2)$$

$$[MBr_2(p\text{-clan})_2]_{(s)} + \text{calorimetric solvent} \rightarrow \text{solution C}, \qquad \Delta_3 H^\circ \quad (3)$$

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

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:

$$MBr_{2(s)} + 2p\text{-clan}_{(s)} \rightarrow [MBr_2(p\text{-clan})_2]_{(s)}, \qquad \Delta_r H^\circ \quad (5)$$

where $\Delta_r H^\circ = \Delta_1 H^\circ + \Delta_2 H^\circ - \Delta_3 H^\circ$, since the final thermodynamic state of reactions (2) and (3) is the same and $\Delta H^\circ = 0$. Table 5 gives the values obtained for the enthalpies of dissolution of MBr_2 ($\Delta_1 H^\circ$), p-clan 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

Table 5
Enthalpies of dissolution at 298.15 K

Compound	Calorimetric solvent	Number of experiments	i	$\Delta_i H^\circ$ (kJ mol^{-1})
$MnBr_{2(s)}$	Methanol	10	1	−101.40 ± 1.55
p-clan$_{(s)}$	2:1 MBr_2–methanol	4	2	26.86 ± 0.43
$[MnBr_2(p\text{-clan})_2]_{(s)}$	Methanol	4	3	−30.27 ± 0.92
$FeBr_{2(s)}$	Methanol	6	1	−86.24 ± 2.78
p-clan$_{(s)}$	2:1 $FeBr_2$–methanol	4	2	23.78 ± 1.01
$[FeBr_2(p\text{-clan})_2]_{(s)}$	Methanol	5	3	9.18 ± 0.18
$CoBr_{2(s)}$	Methanol	8	1	−108.09 ± 1.29
p-clan$_{(s)}$	2:1 $CoBr_2$–methanol	5	2	25.59 ± 0.53
$[CoBr_2(p\text{-clan})_2]_{(s)}$	Methanol	5	3	−26.05 ± 1.23
$NiBr_{2(s)}$	1.2 M HCl[a]	7	1	−73.87 ± 0.94
p-clan$_{(s)}$	2:1 $NiBr_2$–1.2 M HCl[a]	6	2	−12.77 ± 0.60
$[NiBr_2(p\text{-clan})_2]_{(s)}$	1.2 M HCl[a]	4	3	−26.47 ± 0.24
$CuBr_{2(s)}$	25% 1.2 M HCl–methanol[b]	5	1	−25.41 ± 0.23
p-clan$_{(s)}$	2:1 $CuBr_2$–25% 1.2 M HCl–methanol[b]	4	2	−4.50 ± 0.15
$[CuBr_2(p\text{-clan})_2]_{(s)}$	25% 1.2 M HCl–methanol[b]	5	3	13.96 ± 0.11
$ZnBr_{2(s)}$	Methanol	8	1	−49.20 ± 0.42
p-clan$_{(s)}$	2:1 $ZnBr_2$–methanol	4	2	26.94 ± 0.14
$[ZnBr_2(p\text{-clan})_2]_{(s)}$	Methanol	4	3	26.90 ± 1.27

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

4–10 replicate measurements. The electronic spectra reveled that the Mn(II) and Ni(II) adducts exist as polymers in the solid phase, with bridges of bromide ions linking the metallic ions [8]. The thermochemical parameters were calculated for hypothetical monomeric adducts in the solid phase for these adducts. From the values obtained for the standard enthalpies of the acid/base reactions ($\Delta_r H^\circ$) and by using appropriate thermochemical cycles [14,32,33], 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 metal–nitrogen bonds [33] being equal to $(\bar{D}_{(M-N)}) = -\Delta_r H^\circ(g)/2$. Table 6 lists the values for all these thermochemical parameters.

For the determination of $\Delta_r H^\circ(g)$ it was necessary to assume that the molar standard enthalpies of the adducts were equal to the enthalpy of sublimation of one mol of the ligand [33,36] 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 obtained for the adducts, the acidity order of the salts can be obtained: $FeBr_2 > NiBr_2 > CoBr_2 > ZnBr_2 > MnBr_2 > CuBr_2$. Using the $(\bar{D}_{(M-N)})$ values, the order is: $FeBr_2 > MnBr_2 > CoBr_2 > NiBr_2 > CuBr_2 > ZnBr_2$. Comparing these $(\bar{D}_{(M-N)})$ values with the values obtained for aniline adducts of the same metal(II) bromides with the same stoichiometry [11], it is observed the basicity order: p-chloroaniline < aniline, as would be expected on the basis of the inductive effect by the substitution of one hydrogen atom in the phenyl group of aniline, by the electron withdrawing chlorine atom, leading to the

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

Compound	$\Delta_r H^\circ$	$\Delta_f H^\circ$	$\Delta_s^g H^\circ$	$\Delta_M H^\circ$	$\Delta_D H^\circ$	$\Delta_r H^\circ(g)$	$D_{(M–N)}$
$MnBr_{2(s)}$		−384.9[a]	206[a]				
$FeBr_{2(s)}$		−249.8[a]	204[a]				
$CoBr_{2(s)}$		−220.9[a]	183[a]				
$NiBr_{2(s)}$		−212.1[a]	170[a]				
$CuBr_{2(s)}$		−141.8[a]	182.4[a]				
$ZnBr_{2(s)}$		−328.65[a]	159.7[a]				
p-clan$_{(s)}$		−39.4[b]	90.5[b]				
$[MnBr_2(p\text{-clan})_2]_{(s)}$	−44.27 ± 1.85	−508.0 ± 3.4		−431.2 ± 4.8	225.3 ± 2.7	−340.7 ± 5.2	170.4 ± 2.6
$[FeBr_2(p\text{-clan})_2]_{(s)}$	−71.64 ± 2.96	−400.2 ± 4.1		−457 ± 5	252.6 ± 5.0	−366 ± 6	183 ± 3
$[CoBr_2(p\text{-clan})_2]_{(s)}$	−56.45 ± 1.86	−356.2 ± 3.4		−420 ± 3	237.5 ± 2.7	−330 ± 4	165 ± 2
$[NiBr_2(p\text{-clan})_2]_{(s)}$	−60.17 ± 1.14	−351.1 ± 2.5		−411.3 ± 4.3	241.2 ± 4.2	−320.8 ± 4.7	160.4 ± 2.4
$[CuBr_2(p\text{-clan})_2]_{(s)}$	−43.87 ± 0.30	−343.6 ± 2.8		−407.3 ± 4.1	224.9 ± 4.0	−316.8 ± 4.6	158.4 ± 2.3
$[ZnBr_2(p\text{-clan})_2]_{(s)}$	−49.16 ± 1.34	−456.6 ± 3.1		−389.9 ± 3.1	131.8 ± 2.4	−299.4 ± 3.3	149.7 ± 1.7

[a] See Ref. [34].
[b] See Ref. [35].

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

Compound	$\Delta_f H^\circ$	$\Delta_r H^\circ$	$\Delta_{fi} H^\circ$
$Br_{(g)}{}^-$	-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]		
$Cu_{(g)}{}^{2+}$	3054.5 ± 2.1[b]		
$Zn_{(g)}{}^{2+}$	2781.0 ± 0.4[b]		
$[MnBr_2(p\text{-clan})_2]_{(g)}$	-418 ± 6	-340.7 ± 5.2	-2605 ± 7
$[FeBr_2(p\text{-clan})_2]_{(g)}$	-310 ± 7	-366 ± 6	-2726 ± 8
$[CoBr_2(p\text{-clan})_2]_{(g)}$	-266 ± 5	-330 ± 4	-2772 ± 6
$[NiBr_2(p\text{-clan})_2]_{(g)}$	-261 ± 5	-320.8 ± 4.7	-2856 ± 6
$[CuBr_2(p\text{-clan})_2]_{(s)}$	-174.0 ± 5.4	-316.8 ± 4.6	-2892.6 ± 6.4
$[ZnBr_2(p\text{-clan})_2]_{(g)}$	-366.2 ± 4.0	-299.4 ± 3.3	-2811.3 ± 4.9

[a] Ref. [37].
[b] Ref. [38].

decrease of the electronic density on the nitrogen atom of aniline.

The enthalpy changes for the processes of hypothetical adduct formations in the gaseous phase from metal(II) ions, bromide ions and *p*-chloroaniline molecules can be evaluated:

$$M_{(g)}{}^{2+} + 2Br_{(g)}{}^{-} + 2p\text{-clan}_{(g)} \rightarrow [MBr_2(p\text{-clan})_2]_{(g)}, \qquad \Delta_{fI} H^\circ \tag{6}$$

with $\Delta_{fI}H^\circ = \Delta_f H^\circ(\text{adduct}_{(g)}) - \Delta_f H^\circ(M_{(g)}{}^{2+} - 2\,\Delta_f H^\circ(Br_{(g)}{}^{-}) - \Delta_f H^\circ(p\text{-clan}_{(g)})$.

Table 7 lists the values obtained for these enthalpy values.

The environment around the Mn(II) ions in the solid state is pseudo-tetrahedral only in the cases of Fe(II), Co(II) and Cu(II) ions, as different atoms (two bromide ions and two nitrogen atoms) are present. Supposing than in the gaseous phase, all the metal ions studied here are pseudo-tetrahedrally surrounded by two bromide ions and two nitrogen atoms, it is possible and better to find correlations of the $\Delta_{fI}H^\circ$ values rather than to get correlations of the ($\bar{D}_{(M-N)}$) values. The correlation with the metal atomic number is present in the Fig. 1. It is seen part of the double periodic variation profile of the first series of the transition elements. 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 variation of the enthalpies values is linear in a hypothetical state without the influence of the ligand field. In such a case 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) (129 kJ/mol) > Cu(II) (125 kJ/mol) > Co(II) (87 kJ/mol) > Fe(II) (78 kJ/mol). This is nearly the same order obtained for comparable adducts of aniline [11], only with the inversion of the Co(II) and Fe(II) ions.

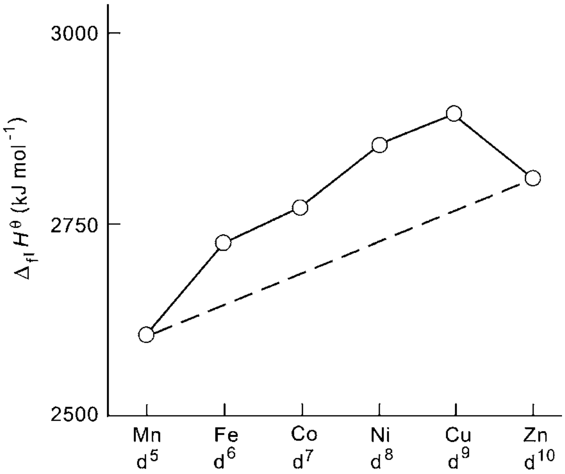

Fig. 1. Plot of the enthalpy changes of complex formation in the gaseous phase from ionic components against d-electron configuration.

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