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Thermochemistry of adducts of some bivalent transition metal bromides with quinoline

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Abstract

The compounds [$MBr_2(quin)_n$] (where M is Mn(II), Co(II), Ni(II), Cu(II) or Zn(II); quin, quinoline; $n = 1$ or 2) 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 quinoline in methanol or 1.2 M aqueous HCl were measured and by using thermochemical cycles, the following 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 M(II)–nitrogen bonds ($\bar{D}_{(M\text{–}N)}$) have been estimated as well as the enthalpies of adduct formation in the gaseous phase.

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

1. Introduction

Quinoline is known to form complexes with transition metal(II) halides [1–13]. Thermochemical parameters related to the transition metal-nitrogen coordinated bonds formed in these compounds are not found in the literature.

The main purpose of the present article is the calorimetric determination of the energy involved in the formation of the coordinated metal-nitrogen bonds as well as to determine several termochemical parameters for the adducts formed between several metal(II) bromides with quinoline. The thermochemical properties of these compounds helps the understanding of the coordinated metal(II)-nitrogen bonds formed. The characterization of the thermodynamic properties of these compounds eventually could be used in determining their potential applications in catalysis and in the chromatographic separation of the metallic ions.

2. Experimental

2.1. Chemicals

Quinoline (98%, Aldrich) was purified by distillation with an efficient column and stored over 4 Å molecular sieves (111–112 °C/2–20 mm Hg). All the anhydrous metal(II) bromides used in the preparation of the adducts were of reagent grade (99% +). Solvents used in the synthesis of the compounds and in calorimetric measurements were purified by distillation and stored over Linde 4 Å molecular sieves.

2.2. Adducts synthesis

The adducts were prepared by the reaction of the solutions of the metal(II) bromides in ethanol with quinoline (for $FeBr_2$ quinoline was used as the solvent). In nearly all cases it was used a molar ratio salt/ligand of nearly 1/4 was used. Petroleum ether was used for washing the compounds obtained. A typical procedure is given below.

2.2.1. $CuBr_2$–quinoline

To a solution of 1.2 g of $CuBr_2$ (5.37 mmol) in 80 mL of hot ethanol, 2.6 mL (21 mmol) of quinoline was slowly added drop-

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wise under stirring. The green solid that formed was filtered and washed with three portions of petroleum ether. The product was dried for several hours in vacuum and stored in a desiccator over calcium chloride.

2.3. 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 of the aqueous solution of the adducts [14]. Bromine analyses were obtained by gravimetry with standard 0.1 M $AgNO_3$ solution, after the adducts had been dissolved in water [15]. The capillary melting points of the adducts were determined with an UNIMELT equipment from Thomas Hover.

2.4. Infrared spectra

Spectra were obtained with samples in KBr matrix for the solid adducts. For quinoline, a film of the ligand sandwiched between KBr plates was used. 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 with a Bomem FT DA8 spectrophotometer with sample nulls of the adducts in nujol sandwiched between polyethylene plates.

2.5. Thermal studies

TG/DTG and DSC measurements were obtained in argon atmosphere in a Du Pont 951 TG analyzer with the samples varying in mass from 7.85 to 26.48 mg (TG/DTG) and from 3.66 to 11.25 mg (DSC) and a heating rate of 10 K min^{-1} in the 298–678 K (DSC) and 298–1248 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, $\Delta_{s}{}^{l}H^{\circ} = 28.4\ J\ g^{-1}$).

2.6. Calorimetric measurements

All the solution calorimetric measurements were carried out in an LKB 8700-1 calorimeter as described before [16]. The solution calorimetric measurements were performed by dissolving samples of 5.2–80.2 mg of the adducts or metal(II) bromides in 100 mL of methanol or 1.2 M aqueous HCl and the ligand quinoline in this last solution maintaining a molar relation salt/ligand equal to the stoichiometry of the adduct. The accuracy of the calorimeter was cheeked by determining the heat of dissolution of tris[(hydroxymethyl)amino]methane in 0.1 mol dm^{-3} HCl. The result (-29.78 ± 0.03 kJ mol^{-1}) is in agreement with the value recommended by IUPAC (-29.763 ± 0.003 kJ mol^{-1}) [17].

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 adduct of $FeBr_2$ showed an indefinite stoichiometry despite the fact it was synthesized with a greater excess of quinoline. The yields range from 70 to 97%. The yields, melting points, colors, appearance and analytical data are summarized in Table 1.

3.1. Infrared spectra

The more important IR bands of the compounds are reported in Table 2. The spectra show shift of several bands after coordination with respect to the free ligand. The IR data can be interpreted in terms of the coordination of quinoline through its nitrogen atom [13]. The stretching modes M–N and M–Br were assigned in the low frequency IR region for all the adducts [10,18].

3.2. Thermal studies

Thermogravimetry and derivative thermogravimetry of the adducts showed that the thermal dissociation processes were of different types. The adducts of Co and Zn lose all the ligand in the first two steps of mass loss followed by the decomposition of MBr_2. The Co adduct left a residue with metal content. The adduct of Mn lost part of the ligand in the first step of mass loss followed by the loss of the rest of the ligand and the decompo-

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

Compound	Yield	Melting point (K)[a]	Appearance[b]	C		H		N		M		Br	
				Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
$[MnBr_2(quin)]$	78	409	l. bro. pw.	31.43	31.51	2.05	2.13	4.07	4.17	15.97	15.92	46.47	46.46
$[CoBr_2(quin)_2]$	92	589–90	bl. cr.	45.32	45.25	2.96	2.70	5.87	5.89	12.35	12.31	33.50	33.49
$[NiBr_2(quin)_2]$	97	436–8	d. bl. cr.	45.34	45.50	2.96	3.09	5.87	5.86	12.31	12.29	33.52	33.49
$[CuBr_2(quin)_2]$	81	476–8	bro. gr. pw.	44.88	44.64	2.93	2.84	5.82	5.75	13.19	13.20	33.18	33.20
$[ZnBr_2(quin)_2]$	70	553–4	wh. pw.	44.71	44.67	2.92	2.88	5.79	5.67	13.52	13.49	33.05	33.01

[a] Melting with decomposition.

[b] Key: l., light; d., dark; bl., blue; gr., green; wh., white; bro., brownish; pw., powder; cr., crystals.

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

quin	$[MnBr_2(quin)]$	$[CoBr_2(quin)_2]$	$[NiBr_2(quin)_2]$	$[CuBr_2(quin)_2]$	$[ZnBr_2(quin)_2]$	Assignment
1596s	1593s	1584m	1594s	1582m	1585m	$\nu_{(c–c)}$
1031m	977m	992m	956m	1019m	960m	Ring
n.o.	797vs	792vs	780vs	782vs	782vs	$\phi_{(c–c)}$
				399m	400s	$\nu_{(M–N)}$
	233s	263m, 249m, 239m	241m	263s	239s	$\nu_{(M–Br)}$
	207m		205s		220s	$\nu_{(M–N)}$
	192m	193m	196s	199w	206m	$\nu_{(M–N)}$

Key: ν, stretching; Ring, ring breathing; ϕ, ring deformation out of plane.

[a] Intensity of bands: vs, very strong; s, strong; m, medium; w, weak; n.o., not observed.

sition of $MnBr_2$ in two more steps of mass loss. A residue with metal content is observed. The adduct of Ni loses part of ligand in the first two steps of mass loss followed by the loss of the rest of the ligand and part of the bromine in the third step. In the fourth step is eliminated the rest of bromine and part of the metal content leaving a residue with metal content. The adduct of Cu loss mass in two steps, the first with elimination of all the ligand and the decomposition of $CuBr_2$. The intermediate compound that formed is decomposed in the second step giving no residue.

The DSC curves of the adducts are consistent with the TG/DTG data and show endothermic peaks due to fusion, partial elimination of ligand or decomposition with partial elimination of the ligand and bromine. Strongly exothermic peaks due to the redox decomposition of MBr_2 are also observed. Table 3 presents the thermoanalytical data of the adducts.

3.3. Electronic spectra

The ligand field parameters for the Co adduct were calculated according to Lever [19]. Considering the number and position of the bands [20,21] and according with the magnitude of the crystal field parameters as compared with that of Bolster [22], it is concluded that the adduct of Co(II) is pseudo-octahedrally surrounded by two nitrogen atoms from two ligand molecules and by four bromide ions in a polymeric structure of bridging halide ions. In addition, a strong band at 15,448 cm^{-1} is observed that is associated with the presence of terminal tetrahedral units of the octahedral polymeric chains, with Co(II) being pseudo-tetrahedrally surrounded by two bromide ions and two nitrogen atoms from two quinoline molecules. The ligand field parameters for the Ni(II) adduct were calculated according to Reedijk et al. [23] 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 Bolster [22], 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 bridge structure. For the Mn(II) adduct since only spin-forbidden bands can be observed in the electronic spectra of high-spin Mn(II) compounds, it is not possible to determine with accuracy the ligand field parameters. It

Table 3
Thermal data of the compounds

Compound	Mass lost (%)		TG temperature range (K)	Species lost	DSC peak	ΔH° ($kJ\,mol^{-1}$)
	Calculated	Observed				
$[MnBr_2(quin)]$	18.78	15.52	348–464	−0.5quin	385	133.4
	25.75	28.98	464–545	−0.5quin–0.3Br	458	10.4
	39.50	39.49	907–1003	−1.7Br	589	56.6
		16.01[a]				
$[CoBr_2(quin)_2]$	27.08	30.11	477–548	−quin	529	49.8
	27.08	30.11	548–565	−quin		
	38.44	36.71	887–954	−2Br–0.4Co		
		7.07[a]				
$[NiBr_2(quin)_2]$	13.53	11.00	360–393	−0.5quin	388	57.3
	27.08	24.94	393–472	−quin	490	40.1
	21.92	24.09	472–532	−0.5quin–0.5Br	570	5.61
	32.54	34.66	928–994	−1.5Br–0.6Ni	589	8.97
		5.31[a]			602	7.65
$[CuBr_2(quin)_2]$	66.08	67.22	378–495	−2quin–0.75Br	491	40.6
	33.92	32.48	784–853	−1.25Br–Cu	592	−275.9
$[ZnBr_2(quin)_2]$	26.72	26.99	470–482	−quin	516	45.2
	26.72	25.14	482–577	−quin	644	−49.1
	46.56	48.20	577–735	−2Br–Zn		

[a] Residue at 1248 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
[$MnBr_2$(quin)]	17.5, 25.6	27.4, 33.8

Compound	Band maxima ($\times 10^3$ cm^{-1})							
	d–d							Intraligand + charge transfer
	ν_1	ν_2	ν_3	D_q (cm^{-1})	B (cm^{-1})	D_q/B	β[a]	
[$CoBr_2(quin)_2$]	8.81[b]	18.81[b]	23.10[b]	1001	1045	0.958	1.076	24.2, 26.0, 33.8
		7.27[c]	15.44[c]	425	665	0.639	0.685	
[$NiBr_2(quin)_2$]	9.55[d]	15.97[d]	25.1[d]	955	1097	0.871	1.065	34.1

Compound	Band maxima ($\times 10^3$ cm^{-1})	
	d–d	Intraligand + charge transfer
[$CuBr_2(quin)_2$]	16.5	23.6, 34.6

[a] $\beta = B/B_0$; $B_0 = 971$ cm^{-1} (Co^{2+}); $B_0 = 1030$ cm^{-1} [22].
[b] $\nu_1 = {}^4T_{2g} \leftarrow {}^4T_{1g}(F)$; $\nu_2 = {}^4A_{2g} \leftarrow {}^4T_{1g}(F)$; $\nu_3 = {}^2P, {}^2G, {}^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$.
[c] $\nu_2 = {}^4T_1(F) \leftarrow {}^4A_2$; $\nu_3 = {}^4T_1(P) \leftarrow {}^4A_{2g}$.
[d] $\nu_1 = {}^3T_{2g} \leftarrow {}^3A_{2g}$; $\nu_2 = {}^3T_{1g}(F) \leftarrow {}^3A_{2g}$; $\nu_3 = {}^3T_{1g}(P) \leftarrow {}^3A_{2g}$.

Table 5
Enthalpies of dissolution at 298.15 K

Compound	Calorimetric solvent	Number of experiments	$\Delta_i H^\circ$ (kJ mol^{-1} of M^{2+})
$MnBr_{2(s)}$	Methanol	13	−98.43 ± 1.21
quin$_{(l)}$	1:1 $MnBr_2$:methanol	4	−2.23 ± 0.10
[MBr_2(quin)]$_{(s)}$	Methanol	4	−29.87 ± 1.09
$CoBr_{2(s)}$	Methanol	8	−112.91 ± 1.00
quin$_{(l)}$	2:1 $CoBr_2$:methanol	4	−5.16 ± 0.15[a]
[$CoBr_2(quin)_2$]$_{(s)}$	Methanol	5	−21.26 ± 0.70
$NiBr_{2(s)}$	1.2 M aqueous HCl	7	−74.32 ± 0.67
quin$_{(l)}$	2:1 $NIBr_2$:1.2 M aqueous HCl	5	−53.04 ± 2.25[a]
[$NiBr_2(quin)_2$]$_{(s)}$	1.2 M aqueous HCl	5	−42.57 ± 0.79
$CuBr_{2(s)}$	Methanol	9	−36.21 ± 0.43
quin$_{(l)}$	2:1 $CuBr_2$:methanol	4	−6.83 ± 0.30[a]
[$CuBr_2(quin)_2$]$_{(s)}$	Methanol	4	40.53 ± 0.38
$ZnBr_{2(s)}$	Methanol	8	−51.66 ± 0.57
quin$_{(l)}$	2:1 $ZnBr_2$:methanol	4	−5.92 ± 0.18 [a]
[$ZnBr_2(quin)_2$]$_{(s)}$	Methanol	4	37.76 ± 3.68

[a] Per two moles of quinoline.

is, however, possible to deduce the local symmetry, which is pseudo-octahedral [21,22], with two nitrogen atoms from two ligand molecules and four bromide ions surrounding the Mn(II) ion in a bridge structure [24]. For the Cu(II) adduct, the electronic spectrum showed a rather broad asymmetrical band with maxima at 16,528 cm^{-1}. Its intensity and position correspond with those observed for pseudo-octahedral compounds [22], with the Cu(II) ion being surrounded by two nitrogen atoms from two ligand molecules and by four bromide ions, in a bridge structure. 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, quinoline and adducts were obtained as previously reported [16]. The standard enthalpies of dissolution were obtained according to the standard enthalpies of the following reactions in solution:

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

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

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

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

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:

$$MBr_{2(s)} + n\,\text{quin}_{(l)} \rightarrow [MBr_2(\text{quin})_n]_{(s)}, \quad \Delta_r H^\circ \tag{5}$$

Table 6
Summary of the thermochemical results(kJ mol^{-1}) at 298.15 K for the metal(II) bromides and their adducts

Compound	$\Delta_r H^\circ$	$\Delta_f H^\circ$	$\Delta_{s,1g} H^\circ$	$\Delta_M H^\circ$	$\Delta_D H^\circ$	$\Delta_r H^\circ$(g)	$\bar{D}_{(M-N)}$
$MnBr_{2(s)}$		−384.9[a]	206[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]				
$quin_{(l)}$		141.22 ± 0.92[b]	59.32 ± 0.20[b]				
$[MnBr_2(quin)]$	−70.79 ± 1.63	−173.3 ± 3.2		−336.0 ± 2.6	130.11 ± 1.64	−276.7 ± 2.6	138.4 ± 1.3
$[CoBr_2(quin)_2]$	−96.81 ± 1.23	−35.3 ± 2.9		−398 ± 2	215.45 ± 1.29	−339 ± 2	170 ± 1
$[NiBr_2(quin)_2]$	−84.79 ± 2.48	−14.5 ± 3.2		−373.5 ± 2.7	33.85 ± 2.51	−314.2 ± 2.7	157.1 ± 1.4
$[CuBr_2(quin)_2]$	−83.57 ± 0.65	−22.03 ± 2.79		−384.6 ± 1.3	202.21 ± 0.76	−325.3 ± 1.2	162.7 ± 0.6
$[ZnBr_2(quin)_2]$	−95.34 ± 3.73	−141.55 ± 4.62		397 ± 4	213.98 ± 3.75	−338 ± 4	169 ± 2

[a] Ref. [27].
[b] Ref. [28].

where $\Delta_r H^\circ = \Delta_1 H^\circ + \Delta_2 H^\circ - \Delta_3 H^\circ$ since the final thermodynamic state of reaction (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 ($\Delta_1 H^\circ$), quin 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 4–13 replicate measurements. Electronic spectra revealed that nearly all the adducts exist as polymers in the solid phase, with bridges of bromide linking the metallic ions [18,24]. The thermochemical parameters were calculated for hypothetical monomeric adducts. From the values obtained for the standard enthalpies of the acid/base reactions ($\Delta_r H^\circ$) and by using appropriate thermochemical cycles [16,25,26], 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 [26], being equal to $\bar{D}_{(M-N)} = -\Delta_r H^\circ(g)/n$. Table 6 lists the values obtained 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 sublimation of the adducts were equal to the enthalpy of vaporization of one mol of the ligand [26,29] as the melting points and/or the 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: $CoBr_2 > ZnBr_2 > NiBr_2 > CuBr_2 > MnBr_2$. Using the $\bar{D}_{(M-N)}$ values, the order is: $CoBr_2 > ZnBr_2 > CuBr_2 > NiBr_2 > MnBr_2$. The enthalpies for the process of a hypothetical complex formation in the gaseous phase, from metal(II) ions, bromide ions and quinoline molecules can be evaluated:

$$M_{(g)}{}^{2+} + 2Br_{(g)}{}^{-} + n\,\text{quin(g)} \rightarrow [MBr_2(\text{quin})_n]_{(g)}, \quad \Delta_{fl} H^\circ \tag{6}$$

where $\Delta_{fl} H^\circ = \Delta_f H^\circ(\text{adduct(g)}) - \Delta_f H^\circ(M_{(g)}{}^{2+}) - 2\Delta_f H^\circ(Br_{(g)}{}^{-}) - n\Delta_f H^\circ(\text{quin}_{(g)})$

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

Compound	$\Delta_f H^\circ$	$\Delta_r H^\circ$	$\Delta_{fl} H^\circ$
$Br_{(g)}{}^{-}$	−219.07[a]		
$Mn_{(g)}{}^{2+}$	2522.0 ± 0.1[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]		
$[MnBr_2(quin)]_{(g)}$		276.7 ± 2.6	−2539 ± 4
$[CoBr_2(quin)_2]_{(g)}$		−339 ± 2	−2781 ± 5
$[NiBr_2(quin)_2]_{(s)}$		−314.2 ± 2.7	−2848 ± 5
$[CuBr_2(quin)_2]_{(g)}$		−325.3 ± 1.2	−2901.0 ± 4.3
$[ZnBr_2(quin)_2]_{(g)}$		−338 ± 4	−2850 ± 5

[a] Ref. [30].
[b] Ref. [31].

Table 7 lists the values obtained for these enthalpy values. Supposing that in the gaseous phase all the ions are pseudo-tetrahedral it is possible to find correlations of the $\Delta_{fl} H^\circ$ values. The correlation of these enthalpy changes with the metal atomic number is present in Fig. 1. It is seen part of the double periodic variation profile. The correlation between the formation enthalpies of Mn(II), Co(II), Ni(II) and Cu(II) and Mn(II)

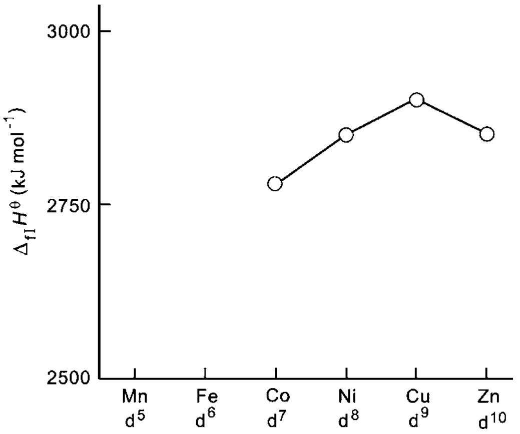

Fig. 1. Plot of the enthalpy changes of complex formation in the gaseous phase from ionic components against d-electron configuration.

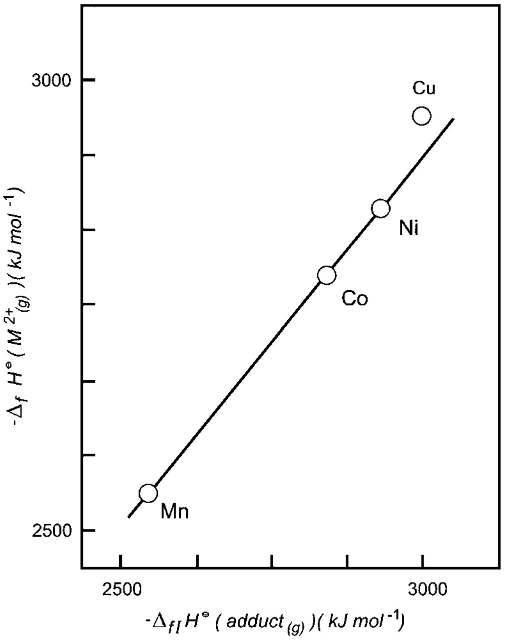

Fig. 2. Plot of the enthalpy changes of metal(II) gaseous ion formation against the enthalpy changes of the respective complex formation in the gaseous phase.

gaseous ions and the formation enthalpies of the respective adduct in the gaseous phase is linear. It is showed in Fig. 2.

The mean bond dissociation enthalpies of the M–N bonds in quinoline complexes are nearly the same as those observed for comparable adducts of Co(II), Ni(II) and Cu(II) bromides with pyridine [32].

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2007.11.018.

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