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Thermochemistry of adducts of some bivalent transition metal bromides with pyridine

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Abstract

The compounds [$MBr_2(py)_2$] (where M is Mn(II), Co(II), Ni(II), Cu(II) or Zn(II); py = pyridine) 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 pyridine in 25% (v/v) 1.2 M aqueous HCl in 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 reactions ($\Delta_r H^\theta$), 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 reactions in the gaseous phase ($\Delta_r H^\theta(g)$). The mean bond dissociation enthalpies of the M(II)-nitrogen bonds have been estimated as well as the enthalpies of the adducts formation in the gaseous phase.

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

1. Introduction

The transition metal(II) of the first row halides or pseudo halides are known to form complex compounds with pyridine and substituted pyridines, with a general formula: $MX_2$2py. They are useful in the separation and purification of certain organic compounds, as well as, they are used in catalysis. In the early sixties and seventies of the last century, they have been extensively studied. In the literature is reported their synthesis, spectroscopy in the UV–vis and infrared regions, thermal studies, structure and studies in solution [1–11]. But the thermochemical parameters related to the transition metal–nitrogen coordinated bonds formed in these compounds are not found in the literature.

The present article is a calorimetric study of the adducts of some bivalent transition metal bromides with pyridine, with the purpose of determining the energy involved in the formation of the coordinated metal–nitrogen bonds and to determine several thermochemical parameters for the adducts. It is important to know the thermodynamic properties of these compounds as far as, this data could be used for understanding the coordinated bonds formed and founding potential applications in catalysis or in the chromatographic separation of the metallic ions.

2. Experimental

2.1. Chemicals

Pyridine (ACS Reagent) was purified by distillation through an efficient column and stored over 4 Å molecular sieves. All the anhydrous metal(II) bromides used in the preparation 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 [12] of the aqueous solution of the adduct samples. Bromine analysis was obtained by gravimetry using standard 0.1 M $AgNO_3$ aqueous solution, after the adducts had been dissolved

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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 solutions of the metal(II) bromides in ethanol with pyridine. In all cases it was used a molar ratio salt/ligand of nearly 1/2. In the case of iron(II) bromide it was used the pyridine itself as the solvent. The obtained solid compounds were filtered and washed with *n*-hexane. A typical procedure is given below.

To a solution of 1.0 g of $NiBr_2$ (4.58 mmol) in 50 mL of ethanol, 1 mL of pyridine (12.36 mmol) was slowly added dropwise under stirring. The yellow 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 FT-IR spectrophotometer in the 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 10.20 to 10.96 mg (TG/DTG) and from 1.68 to 7.82 mg (DSC) and a heating rate of 10 K min^{-1} in the 298–578 K (DSC) and 298–1173 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, $\Delta_{s}{}^{1}H^{\theta} = 28.4\ \mathrm{J\,g^{-1}}$).

2.6. 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.

2.7. Calorimetric measurements

All the solution calorimetric measurements were carried out in an LKB 9700-1 precision calorimeter as described before [14]. The solution calorimetric measurements were performed by dissolving samples of 4.6–105.7 mg of the adducts or metal(II) bromides in 100 mL of 25% (v/v) aqueous 1.2 M HCl in methanol and the ligand pyridine in this last solution maintaining the molar 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 $29.78 \pm 0.03\ \mathrm{kJ\,mol^{-1}}$ is in agreement with the value recommended by IUPAC ($-29.763 \pm 0.003\ \mathrm{kJ\,mol^{-1}}$) [15].

3. Results and discussion

All the adducts were obtained in the solid state. The adduct of $FeBr_2$ with pyridine showed an indefinite stoichometry spite the fact to have been synthesized with a great excess of pyridine. The yields range from 52 to 88%. The yield, melting points, colors, appearance and analytical data are summarized in Table 1.

3.1. Infrared spectra

The infrared spectra of the adducts show dislocation and splitting of several bands when compared with the spectrum of free pyridine, although the patterns are similar. Qualitatively the coordinated pyridine is distinguished from free pyridine by the presence of a weak band in the 1221–1216 cm^{-1} region and by dislocation to higher frequencies of bands at 1590 and 598 cm^{-1} [1]. The similarity of the spectra of coordinated pyridine shows that the electronic density is the same in the aromatic ring since significant changes in the electronic density would produce large changes in the infrared spectra [16–20]. Table 2 presents the main infrared bands of pyridine and its adducts.

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 (Co, Cu and Zn adducts) or three steps (Mn and Ni adducts). They lose all the ligand in the first step (Co, Ni and Zn adducts) or all the ligand in the first two steps (Mn adduct) or all the ligand and

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

Compound	Yield	mp (K)[a]	Appearance[b]	C		H		N		Br		M	
				Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
$[MnBr_2(py)_2]$	69	290–292	l. pi. pw.	32.20	31.99	2.70	2.72	7.51	7.30	14.73	14.65	42.85	42.71
$[CoBr_2(py)_2]$	75	191–192	l. bl. cr.	31.86	30.72	2.67	2.66	7.43	7.31	15.63	15.65	42.40	42.10
$[NiBr_2(py)_2]$	52	184–186	gre. ye. pw.	31.88	31.65	2.68	2.73	7.43	7.28	15.58	15.55	42.42	42.19
$[CuBr_2(py)_2]$	94	98–99	l.gr. pw.	31.48	31.33	2.64	2.66	7.34	7.20	16.65	16.52	41.89	41.71
$[ZnBr_2(py)_2]$	88	203–204	wh. pw.	31.33	31.23	2.63	2.64	7.31	7.26	17.05	16.95	41.69	41.58

[a] Melting with decomposition.
[b] Key: l., light; pi., pink; bl., blue; gre., greenish; ye., yellow; gr., green; wh., white; pw., powder; cr., crystals.

Table 2
Main infrared spectral data[a] for pyridine and its complexes

py	[MnBr$_2$(py)$_2$]	[CoBr$_2$(py)$_2$]	[NiBr$_2$(py)$_2$]	[CuBr$_2$(py)$_2$]	[ZnBr$_2$(py)$_2$]	Assignment
1590sh	1604s	1606s	1606s	1606s	1607s	$\nu_{(CC)}$
1480s	1488m	1486m	1489m	1491s	1488m	$\nu_{(CC, CN)}$
1435vs	1444s	1446s	1445s	1449s	1449s	$\nu_{(CC, CN)}$
	1221m	1216m	1220m	1221m	1218m	
1142s	1154m	1159m	1154m	1154m	1158m	$\nu_{(CC, CN)}$
1063s	1071m	1068m	1073m	1080m	1069s	$\beta_{(CH)}$
1027s	1039m	1045m	1044m	1044m	1044s	ring
990s	1010m	1014m	1014m	1017m	1016m	ring
747vs	752m	759s	756s	756s	758m	$\phi_{(CC)}$
677sh	692s	694s	693s	688s	695s	$\phi_{(CC)}$
598s	628m	643m	634m	642m	640m	$\alpha_{(CCC)}$
no	543m	540m	520m	no	no	$\alpha_{(CCC)}$
no	409m	425m	444m	no	423m	$\phi_{(CC)}$

[a] Intensity of bands: vs, very strong; s, strong; m, medium; sh, shoulder; no, not observed. Key: ν, stretching; β, bending in plane; α, ring deformation in plane; ϕ, ring deformation out of plane; ring, ring breathing.

part of the bromine in the first step (Cu adduct). The adducts of Co, Ni, Cu and Zn lost part of the metal in the last step. In all cases, a residue is observed that is part of the metal [7].

The DSC curves of the adducts are consistent with the TG/DTG data and show strongly endothermic peaks due to the decomposition of the adducts with partial elimination of ligand or ligand and 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 [21]. According to the number and position of the bands [19,22] and considering the magnitude of the crystal field parameters as compared with that of Bolster [23], 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 bromide ions, as it has been also observed by Gill et al. [2]. In addition, the band observed at 15,676 cm^{-1} is associated with the presence of terminal tetrahedral units of the octahedral polymeric chains, with the Co(II) ions being surrounding by two bromide ions and two nitrogen atoms from two pyridine molecules. The ligand parameters for the Ni(II) adduct were calculated according to Reedijk et al. [24] and Lever [21]. According to the number and positions of the observed bands and considering the magnitude of the calculated crystal field parameters as compared with that of Bolster [23], it is concluded that the adduct of Ni(II) is pseudo-octahedrally

Table 3
Thermal analysis data of the compounds

Compound	Mass lost (%)		TG temperature range (K)	Species lost	DSC peak temperature (K)	ΔH^0 (kJ mol^{-1})
	Calculated	Observed				
[MnBr$_2$(py)$_2$]	21.21	21.82	321–445	−py	283	1179
	21.21	20.14	445–530	−py	493	680
	42.85	42.75	827–993	−2Br		
		14.73[a]				
[CoBr$_2$(py)$_2$]	41.98	42.12	324–547	−2py	350	1447
	42.40	47.14	776–963	−2Br–0.35Co	405	18
		10.53[a]			466	287
[NiBr$_2$(py)$_2$]	21.00	24.41	340–465	−py	383	861
	21.00	19.47	465–547	−py	511	866
	45.53	45.25	918–998	−2Br–0.2Ni		
		9.20[a]				
[CuBr$_2$(py)$_2$]	58.22	57.32	323–506	−2py–0.8Br	512	1190
	35.13	36.32	792–877	−1.2Br–0.6Cu	555	856
		7.50[a]				
[ZnBr$_2$(py)$_2$]	41.26	38.97	446–563	−2py	411	17
	55.34	57.67	563–729	−2Br–0.8Zn	493	407
		3.41[a]				

[a] Residue at 1173 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
$[MnBr_2(py)_2]$	19.2, 23.6	32.0, 37.1

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^+	
$[CoBr_2(py)_2]_n$	9.12[a]	19.99[a] 6.81[b]		22.49[a] 15.67[b]	1087 394	947 710	1.147 0.555	0.978 0.731	25.7, 33.1
$[NiBr_2(py)_2]_n$	7.99[c]	12.10[c]	13.71[c]	23.61[c]	799	467	1.000	0.453	28.7, 34.1

Compound	Band maxima ($\times 10^3$ cm^{-1}) d–d
$[CuBr_2(py)_2]_n$	14.2

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

[a] $\nu_1 = {}^4T_{2g} \leftarrow {}^4T_{1g}(F)$; $\nu_2 = {}^4A_{2g} \leftarrow {}^4T_{1g}(F)$; $\nu_3 = {}^2P, {}^2G, {}^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$.

[b] $\nu_2 = {}^4T_1(F) \leftarrow {}^4A_2$; $\nu_3 = {}^4T_1(P) \leftarrow {}^4A_{2g}$.

[c] $\nu_1 = {}^3T_{2g} \leftarrow {}^3A_{2g}$; $\nu_2 = {}^3T_{1g}(F) \leftarrow {}^3A_{2g}$; $\nu_4 = {}^1E_g \leftarrow {}^3A_{2g}$; $\nu_3 = {}^3T_{1g}(P) \leftarrow {}^3A_{2g}$.

surrounded by two nitrogen atoms from two ligand molecules and by four bromide ions in a bridging structure. 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 with accuracy the ligand field parameters. It is however, possible to deduce the local symmetry which is pseudo-octahedral [19,20,23] with two nitrogen atoms from two pyridine molecules and four bromide ions surrounding the Mn(II) ion in a bridging structure [2]. For the Cu(II) adduct the electronic spectrum shows a rather broad asymmetrical band with maxima at 14,215 cm^{-1}. Its intensity and position correspond with those observed for pseudo-octahedral Cu(II) compounds [23], with the Cu(II) ion being surrounded by two nitrogen atoms from two pyridine molecules and by four bromide ions in a bridging structure.

3.4. Calorimetric measurements

The standard enthalpies of dissolution of metal(II) bromides, pyridine 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:

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

$$2py_{(l)} + \text{solution A} \rightarrow \text{solution B}; \quad \Delta_2 H^\theta \tag{2}$$

$$[MBr_2(py)_2]_{(s)} + \text{calorimetric solvent} \rightarrow \text{solution C}; \quad \Delta_3 H^\theta \tag{3}$$

$$\text{SolutionB} \rightarrow \text{solution C}; \quad \Delta_4 H^\theta \tag{4}$$

The application of the 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:

$$MBr_{2(s)} + py_{(l)} \rightarrow [MBr_2(py)_2]_{(s)}; \quad \Delta_r H^\theta \tag{5}$$

since the final thermodynamic 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 ($\Delta_1 H^\theta$), pyridine into the solution of MBr_2 ($\Delta_2 H^\theta$) and of the adducts ($\Delta_3 H^\theta$). Uncertainty intervals given in this table are twice the standard deviation of the means of 4–8 replicate measurements. Electronic spectra reveled that all the adducts (excepted, probably, by the Zn(II) adduct) exist as polymers in the solid state, with bridges of bromide ions linking the metallic ions [2]. The thermochemical parameters for them were calculated for hypothetical monomeric adducts. From the values obtained for the standard enthalpies of the acid/base reactions ($\Delta_r H^\theta$) and by using appropriate thermochemical cycles [14,25,26], 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 mean standard enthalpies of the M–N bonds [26], being equal to $\bar{D}_{(M\text{–}N)} = -\Delta_r H^\theta(g)/2$. 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 were equal to the enthalpy of vaporization of one mol of ligand [26,29] 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 $\Delta_r H^\theta$ values for the adducts, the acidity order of the salts can be established: $CoBr_2 > NiBr_2 > MnBr_2 > CuBr_2 > ZnBr_2$. Using the $\bar{D}_{(M\text{–}N)}$ values, the order is: $MnBr_2 > CoBr_2 > NiBr_2 > CuBr_2 > ZnBr_2$. The enthalpies for

Table 5
Enthalpies of dissolution at 298.15 K

Compound	Calorimetric solvent[a]	Number of experiments	i	$\Delta_i H^{\theta}$ (kJ mol^{-1})
$MnBr_{2(s)}$	25% 1.2 M HCl–methanol	5	1	−76.09 ± 0.82
$py_{(l)}$	2:1 $MnBr_2$–25% 1.2 M HCl–methanol	4	2	−41.63 ± 0.64
$[MnBr_2(py)_2]_{(s)}$	25% 1.2 M HCl–methanol	4	3	−7.00 ± 0.40
$CoBr_{2(s)}$	25% 1.2 M HCl–methanol	8	1	−86.48 ± 0.79
$py_{(l)}$	2:1 $CoBr_2$–25% 1.2 M HCl–methanol	5	2	−38.98 ± 1.29
$[CoBr_2(py)_2]_{(s)}$	25% 1.2 M HCl–methanol	5	3	−8.05 ± 0.62
$NiBr_{2(s)}$	25% 1.2 M HCl–methanol	4	1	−69.30 ± 2.30
$py_{(l)}$	2:1 $NiBr_2$–25% 1.2 M HCl–methanol	4	2	−48.89 ± 0.09
$[NiBr_2(py)_2]_{(s)}$	25% 1.2 M HCl–methanol	5	3	−3.82 ± 0.13
$CuBr_{2(s)}$	25% 1.2 M HCl–methanol	8	1	−20.00 ± 0.29
$py_{(l)}$	2:1 $CuBr_2$–25% 1.2 M HCl–methanol	4	2	−46.62 ± 0.78
$[CuBr_2(py)_2]_{(s)}$	25% 1.2 M HCl–methanol	5	3	33.93 ± 0.74
$ZnBr_{2(s)}$	25% 1.2 M HCl–methanol	4	1	−32.99 ± 0.03
$py_{(l)}$	2:1 $ZnBr_2$–25% 1.2 M HCl–methanol	4	2	−47.89 ± 0.48
$[ZnBr_2(py)_2]_{(s)}$	25% 1.2 M HCl–methanol	5	3	−1.20 ± 0.04

[a] 25% aqueous 1.2 M HCl in methanol.

Table 6
Summary of the thermochemical results (kJ mol^{-1}) for metal(II) bromide adducts

Compound	$\Delta_r H^{\theta}$	$\Delta_f H^{\theta}$	$\Delta_s{}^g H^{\theta}$	$\Delta_M H^{\theta}$	$\Delta_D H^{\theta}$	$\Delta_r H^{\theta}(g)$	$\bar{D}_{(M-N)}$
$MnBr_{2(s)}$		−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]				
$py_{(l)}$		−101.2 ± 0.7[b]	40.2[b]				
$[MnBr_2(py)_2]_{(s)}$	−110.7 ± 1.11	−293.2 ± 2.7		−397.0 ± 3.0	191.1 ± 2.3	−356.8 ± 3.2	178.4 ± 1.6
$[CoBr_2(py)_2]_{(s)}$	−117.41 ± 1.63	−135.9 ± 8.6		−381 ± 3	197.8 ± 3.1	−341 ± 3	171 ± 2
$[NiBr_2(py)_2]_{(s)}$	−114.37 ± 2.31	−124.1 ± 2.9		−364.9 ± 3.2	194.8 ± 3.1	−324.7 ± 3.7	162.4 ± 1.9
$[CuBr_2(py)_2]_{(s)}$	−100.55 ± 1.11	−119.1 ± 2.7		−364 ± 3	181.0 ± 2.3	−323.2 ± 2.7	161.6 ± 1.4
$[ZnBr_2(py)_2]_{(s)}$	−79.68 ± 0.48	−205.9 ± 2.5		−343 ± 3	160.1 ± 2.1	−303 ± 3	151.5 ± 1.5

[a] See [27].
[b] See [28].

the process of a hypothetical complex formation in the gaseous phase from metal(II) ions, bromide ions and pyridine molecules can be evaluated:

$$M_{(g)}{}^{2+} + 2Br_{(g)}{}^{-} + 2py_{(g)} \rightarrow [MBr_2(py)_2](g); \quad \Delta_{fI} H^{\theta} \tag{6}$$

$$\text{With } \Delta_{fI} H^{\theta} = \Delta_f H^{\theta}(\text{adduct}_{(g)}) - \Delta_f H^{\theta}(M_{(g)}{}^{2+}) - 2\Delta_f H^{\theta}(Br_{(g)}{}^{-}) - 2\Delta_f H^{\theta}(py_{(g)})$$

Table 7 lists the values obtained for these enthalpy values. Supposing that in the gaseous phase, all the metallic ions are pseudo-tetrahedrally surrounded it is possible to find correlations of the $\Delta_{fI}H^{\theta}$ 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 $\Delta_{fI}H^{\theta}$ values obtained depend on the electronic structure of the central metallic 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 enthalpy values 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, 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: Cu(II) (174 kJ mol^{-1}) > Ni(II) (124 kJ mol^{-1}) >Co(II) (87 kJ mol^{-1}). The complexes formed by Co(II) and Cu(II) with β-picoNO and α-picoNO with the same stoichiometry

Table 7
Auxiliary data and enthalpy changes of the ionic complex 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]		
$Co_{(g)}{}^{2+}$	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]		
$[MnBr_2(py)_2]_{(g)}$	−253 ± 5	−356.8 ± 3.2	−2620 ± 6
$[CoBr_2(py)_2]_{(g)}$	−96 ± 4	−341 ± 3	−2782 ± 6
$[NiBr_2(py)_2]_{(g)}$	−84 ± 5	−324.7 ± 3.7	−2859 ± 6
$[CuBr_2(py)_2]_{(g)}$	−0.2 ± 4.4	−323.2 ± 2.7	−2899.4 ± 5.6
$[ZnBr_2(py)_2]_{(g)}$	−189 ± 4	−303 ± 3	−2815 ± 5

[a] Reference [30].
[b] Reference [31].

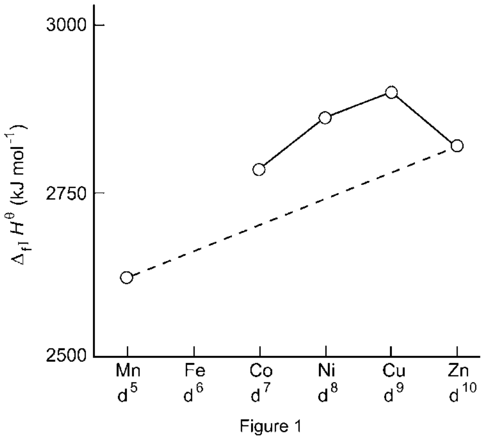

Fig. 1. Plot of the enthalpy changes of complex formation in the gaseous phase from ionic components against d-electron configuration.

[32,33] have the stabilization energies of 72 and 52 kJ mol^{-1} (Co(II)) and 129 and 174 kJ mol^{-1} (Cu(II). This means that the stabilization energies provides by two py molecules is higher that that provides by two β-picoNO molecules or two α-picoNO molecules, being the order: α-picoNO < β-picoNO < py.

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