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Thermochemistry of adducts of some bivalent transition metal bromides with β-picoline N-oxide

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Abstract

The compounds $[MBr_2(L)_2]$ (where M is Mn(II), Fe(II), Co(II), Ni(II), Cu(II) or Zn(II); L = β-picoline N-oxide (β-picoNO)) 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 β-picoNO in methanol or aqueous 1.2 M HCl 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 ($\Delta_r H^\circ$), 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)–oxygen bonds ($\bar{D}_{(M–O)}$) have been estimated.

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

1. Introduction

The standard enthalpies of formation of coordination compounds are important to characterize them and to understand their properties [1]. Thermochemical parameters related to transition metal–oxygen coordinated bonds are limited. Theoretical and practical aspects of complexes formed by transition metal ions are used for determining their potential applications in catalysis or in the chromatographic separation of metals. Then, the knowledge of the thermodynamic properties of the complexes is important. On the other hand, β-picoline N-oxide has been used as a ligand due to its intrinsic ability to coordinate metal cations through its oxygen atom. This chemical property is attributed to its particular electronic configuration [2].

In this paper it is reported the synthesis of complexes of some bromides of divalent 3d electrons elements with β-picoline N-oxide. In the literature it is found the synthesis, characterization by elemental analysis, infrared and electronic spectroscopy and in some cases, by thermal analysis (TG/DTG) of complexes of metal(II) bromides of transition elements, with several substituted pyridine N-oxides [2–14]. But, no information about the enthalpies of the transition element–oxygen coordinated bonds formed in these compounds is given. No any thermochemical study is made on them. The complexes of metal(II) bromides with β-picoline N-oxide were synthesized with the purpose of obtaining several thermochemical parameters for these complexes and to establish correlations among these parameters. Correlations between the bond energies observed in these complexes with the bond energies observed for the adducts of the same metal(II) bromides with pyridine N-oxide [15] are also studied.

2. Experimental

2.1. Chemicals

β-Picoline N-oxide was prepared according with the method of Boekelheide and Linn [16]. All the anhydrous salts 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.

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2.2. Analytical

Carbon, hydrogen and nitrogen were determined by microanalytical procedures. The metal contents were determined by complexometric titration with 0.01 M EDTA solution [17] of the aqueous solution of adduct samples. Bromide analysis was obtained by gravimetry using standard 0.1 $AgNO_3$ solution, after the adducts had been dissolved in water [18]. The capillary melting points of the adducts were determined using a UNIMELT equipment from Thomas Hover.

2.3. Adduct synthesis

The adducts were prepared by the reaction of MBr_2 dissolved in dry ethanol ($CoBr_2$), or dry methanol ($FeBr_2$ or $NiBr_2$) or dry acetone ($MnBr_2$ or $ZnBr_2$) with a solution of β-picoline N-oxide in the same solvent used for dissolving the metal(II) bromide. In all preparations were used a molar ratio salt/ligand of 1/2 with the exception of $CoBr_2$ adduct in which, a relation of 1/3 was used. A typical procedure is given bellow.

To a solution of 2.0 g of $MnBr_2$ (9.3 mmol) in 30 ml of dry acetone, 2.0 g of β-picoNO (18.6 mmol) in 15 ml of dry acetone was added, slowly and dropwise with stirring. The solid formed was filtered and washed with petroleum ether. 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

TG/DTG and DSC measurements were obtained in an argon atmosphere in a Du Pont 951 TG analyzer with samples varying in mass from 3.82 to 8.80 mg (TG/DTG) and from 2.13 to 2.92 mg (DSC) and a heating rate of 10 K min^{-1} in 293–673 K (DSC) and 298–1173 K (TG/DTG) temperature ranges. TG calibration for temperature 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 using metallic indium as a standard (mp = 165.73 °C, $\Delta_s^1 H^\circ = 28.4\ J\ g^{-1}$).

2.6. Calorimetric measurements

All the solution calorimetric determinations were carried out in an LKB 8700-1 precision calorimeter as described elsewhere [19]. The solution calorimetric measurements were performed by dissolving samples of 3.0–66.1 mg of the adducts or metal(II) bromides in 100 ml of methanol or aqueous 1.2 M HCl and the β-picoNO 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 ($-29.763 \pm 0.003\ kJ\ mol^{-1}$) [20].

3. Results and discussion

All the adducts obtained were solids. The yields ranged from 30 to 97%. The yields, melting points, color appearance and analytical data are summarized in Table 1.

3.1. Infrared spectra

The infrared spectra of β-picoNO adducts are similar to that of free ligand except for small shifts and decrease in the intensity of some absorption bands when compared with the spectrum of free β-picoNO. Shifts toward lower frequencies are observed after coordination for the absorption band attributed to the NO stretching vibration in the free ligand. The band attributed to the angular deformation of the group NO (δ_{NO}) is usually unchanged after coordination [2,3,7,21–23]. It is observed here, small shifting to higher frequencies after coordination, probably due to intermolecular steric effects caused by the methyl group on the ring of the ligand [7]. All these facts can be interpreted as evidence of the coordination of β-picoNO through its oxygen atom [19]. The $\nu_{(M–O)}$ bands are assigned in the low frequency IR region, at 422–280 cm^{-1} [5,7] for all the adducts, consistent with the range proposed for $\nu_{(M–O)}$ frequencies of aromatic N-oxides [7] (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 (Cu and Zn adducts), three (Fe adduct), four (Co and Mn adducts) or five (Ni adduct) steps. Some of these steps consist of two successive decomposition processes. They loss part or all the ligand in the first or the first two steps following by the losing of the rest of the ligand, bromine and metal in the next steps. In most cases it is observed a residue, which is probably the respective metal.

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

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

Compound	Yield	mp (K)[a]	Appearance[b]	C		H		N		M		Br	
				Calculated	Found	Calculated	Found	Calculated	Found	Calculated	Found	Calculated	Found
[$MnBr_2$(β-picoNO)$_2$]	97	439–440	ye. pw.	33.29	32.98	3.26	3.25	6.47	6.45	12.69	12.74	36.91	36.97
[$FeBr_2$(β-picoNO)$_2$]	35	337–338	br. pw.	33.22	32.98	3.25	3.23	6.46	6.43	12.87	12.95	36.83	36.93
[$CoBr_2$(β-picoNO)$_2$]	73	349–350	bl. pw.	32.98	33.03	3.23	3.24	6.41	6.43	13.49	13.51	36.57	36.62
[$NiBr_2$(β-picoNO)$_2$]	30	387–389	ye. pw.	33.00	32.99	3.23	3.23	6.41	6.37	13.44	13.42	36.59	36.60
[$CuBr_2$(β-picoNO)$_2$]	46	390–391	d. gr. pw.	32.64	32.70	3.20	3.26	6.34	6.41	14.39	14.29	36.19	36.09
[$ZnBr_2$(β-picoNO)$_2$]	81	384–385	wh. pw.	32.50	32.38	3.18	3.05	6.32	6.29	14.74	14.74	36.04	35.99

[a] Melting with decomposition.

[b] Key: ye., yellow; br., brown; bl., blue; gr., green; wh., white; d., dark; pw., powder.

Table 2
Infrared data for β-picoNO and its complexes

β-picoNO	$[MnBr_2(\beta\text{-picoNO})_2]$	$[FeBr_2(\beta\text{-picoNO})_2]$	$[CoBr_2(\beta\text{-picoNO})_2]$	$[NiBr_2(\beta\text{-picoNO})_2]$	$[CuBr_2(\beta\text{-picoNO})_2]$	$[ZnBr_2(\beta\text{-picoNO})_2]$	Assignment
3073 m	n.o.	3067 m	n.o.	n.o.	3021 m	3057 m	CH str. (ν)
1605 m	1611 m	1609 m	1609 m	1615 m	1609 m	1609 m	CC and CN str. (ν)
1485 m	1492 m	1491 s	1491 s	1491 m	1492 s	1492 s	CC and CN str. (ν)
1455 m	1455 m	1458 m	1459 m	1458 m	1459 s	1424 m	CC and CN str. (ν)
1280 s	1262 s	1261 s	1262 s	1262 s	1252 s	1258 s	NO str. (ν)
1270 sh							
1163 s	1155 s	1160 s	1161 s	1161 s	1158 s	1166 s	CH in-plane def. (β)
1017 s	1018 m	1018 m	1019 m	1020 m	1014 m	1012 m	Ring breathing
948 m	944 m	945 m	944 m	945 m	944 m	941 s	CH out-of-plane def. (γ)
907 w	910 w	911 w	911 w	910 w	900 w	n.o.	CH out-of-plane def. (γ)
794 s	805 s	800 s	801 m	808 s	804 s	798 s	NO bend. (δ)
748 s	749 s	751 s	750 s	750 s	749 s	751 s	CH out-of-plane def. (β)
678 s	676 s	673 m	674 m	n.o.	676 s	674 s	
–	368 s	380 m	384 s	378 sh	381 sh	376 sh	MO str. (ν)
–	331 s	358 m	346 s	358 s	359 s	350 s	
–	213 s	239 m	215 s	222 s	235 s	220 m	MBr str. (ν)
–	197 s	232 m	198 s	203 m	225 sh	207 m	

Key: intensity of bands: w, weak; m, medium; s, strong; sh, shoulder. n.o., not observed.

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 [24]. According to the number and position of the bands [4,7] and considering the magnitude of the crystal field parameters as compared with that of Bol-

Table 3
Thermal analysis data of the compounds $[MBr_2(L)_2]$

Compound	Mass lost (%)		TG temperature range (K)	Species lost	DSC peak temperature	ΔH° (kJ mol^{-1})
	Calculated	Observed				
$[MnBr_2(\beta\text{-picoNO})_2]$	3.47	3.50	342–377	–CH_3	390	4.36
	35.14	34.91[a]	377–564	–CH–NO–L	439	1.91
	11.79	11.63	564–632	–C_4H_3		
	43.26	43.14	802–881	–Br_2–0.5Mn		
		2.89[b]				
$[FeBr_2(\beta\text{-picoNO})_2]$	25.15	27.19	408–449	–L		
	43.61	41.09[a]	449–522	–L–Br		
	22.27	21.77	522–925	–Br–Fe/3		
		9.95[b]				
$[CoBr_2(\beta\text{-picoNO})_2]$	3.44	3.43[a]	332–356	–CH_3	337	2.12
	46.50	45.47	356–567	–L–C_5H_4NO	362	0.06
	31.08	29.99	567–807	–1.7Br		
	18.98	20.42	807–957	–0.3Br–Co		
$[NiBr_2(\beta\text{-picoNO})_2]$	12.38	12.73	381–475	–CH_3–C_3H_3	380	0.59
	37.59	38.43[a]	475–578	–L–C_2HNO	428	4.76
	41.03	41.19	807–884	–Br_2–Ni/3		
	4.44	4.83	884–1050	–Ni/3		
	1.34	1.53	1050–1223	–Ni/10		
		1.29[b]				
$[CuBr_2(\beta\text{-picoNO})_2]$	58.47	58.95	448–516	–2L–0.5Br	341	0.12
	41.53	41.05	516–1008	–1.5Br–Cu	387	2.45
$[ZnBr_2(\beta\text{-picoNO})_2]$	49.22	47.88	531–611	–2L	381	2.32
	49.31	51.11	611–755	–Br_2–0.9Zn		
		1.77[b]				

[a] Two overlapping mass lost.
[b] Residue at 1258 K.

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

Compound	Band maxima ($\times 10^3$ cm^{-1})	
	d–d	Intraligand + charge transfer
[MnBr$_2$(β-picoNO)$_2$]	18.7, 24.5	39.1
[CuBr$_2$(β-picoNO)$_2$]	10.9–15.0[a]	32.2, 23.9

Compound	Band maxima ($\times 10^3$ cm^{-1})		
	d–d		Intraligand + charge transfer
	ν_1[b]	D_q (cm^{-1})	
[FeBr$_2$(β-picoNO)$_2$]	7.62	762	37.0, 20.6

Compound	Band maxima ($\times 10^3$ cm^{-1})			D_q (cm^{-1})	B (cm^{-1})	D_q/B	β^+
	d–d		Intraligand + charge transfer				
	ν_2	ν_3					
[CoBr$_2$(β-picoNO)$_2$]	6.53[c]	14.9[d]	26.5	379	674	0.56	0.69
[NiBr$_2$(β-picoNO)$_2$]	7.28[e]	11.9[f]	26.2	540	899	0.60	0.87

$\beta^+ = B/B_0$; $B_0 = 971$ cm^{-1} (Co^{2+}); $B_0 = 1030$ cm^{-1} (Ni^{2+}) [25].

[a] Very broad band with no distinct maxima.

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

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

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

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

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

ster [25], it is concluded that the adduct of Co(II) is pseudo-tetrahedrally surrounded by two oxygen 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. [26] and Lever [24]. 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 [25], it is concluded that the adduct of Ni(II) is pseudo-tetrahedrally surrounded by two oxygen atoms from two ligand molecules and by two bromide ions. The ligand field parameters for the Fe(II) adduct were calculated according to Bolster [25]. It is concluded by the position of the absorption band and considering the magnitude of D_q that the Fe(II) is pseudo-tetrahedrally surrounded by two oxygen 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 determine with accuracy the ligand-field parameters. It is however, possible to deduce the local symmetry, which is pseudo-tetrahedral [4,25]. For the Cu(II) adduct, the electronic spectrum show a single, rather broad band. In practice, the powder reflectance spectra of tetrahedral cooper complexes can be characterize by a more or less continuous absorption band from 4.0×10^3 to 12.0×10^3 cm^{-1} [25], as it is observed here. The intensity and its position correspond with those observed for pseudo-tetrahedral Cu(II) compounds [5,25], the Cu(II) ion being surrounded by two oxygen atoms from two ligand molecules and by two bromide ions.

3.4. Calorimetric measurements

The standard enthalpies of dissolution of metal(II) bromides, β-picoNO and adducts were obtained as previously reported [19]. The standard enthalpies of dissolution were obtained according to the standard enthalpies of reactions (1)–(4) in solution:

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

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

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

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

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 reaction (5):

$$\mathrm{MBr_{2(s)}} + 2\beta\text{-picoNO}_{(s)} \rightarrow [\mathrm{MBr_2(\beta\text{-}picoNO)_2}]_{(s)}, \quad \Delta_r H^\circ = \Delta_1 H^\circ + \Delta_2 H^\circ - \Delta_3 H^\circ \tag{5}$$

since the final 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$_2$ ($\Delta_1 H^\circ$), β-picoNO 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 4–11 replicate measurements.

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	7	1	-77.96 ± 1.52
β-picoNO$_{(s)}$	2:1 $MnBr_2$–methanol	4	2	-0.48 ± 0.04
$[MnBr_2$(β-picoNO)$_2]_{(s)}$	Methanol	4	3	-2.10 ± 0.13
$FeBr_{2(s)}$	Methanol	5	1	-46.04 ± 0.42
β-picoNO$_{(s)}$	2:1 $FeBr_2$–methanol	4	2	2.60 ± 0.47
$[FeBr_2$(β-picoNO)$_2]_{(s)}$	Methanol	5	3	26.29 ± 1.15
$CoBr_{2(s)}$	Methanol	11	1	-107.30 ± 2.74
β-picoNO$_{(s)}$	2:1 $CoBr_2$–methanol	5	2	-2.14 ± 0.08
$[CoBr_2$(β-picoNO)$_2]_{(s)}$	Methanol	5	3	-24.19 ± 0.89
$NiBr_{2(s)}$	1.2 M HCl[a]	6	1	-71.77 ± 1.05
β-picoNO$_{(s)}$	2:1 $NiBr_2$–1.2 M HCl[a]	4	2	-26.17 ± 0.62
$[NiBr_2$(β-picoNO)$_2]_{(s)}$	1.2 M HCl[a]	6	3	-4.99 ± 0.25
$CuBr_{2(s)}$	Methanol	8	1	-39.66 ± 0.52
β-picoNO$_{(s)}$	2:1 $CuBr_2$–methanol	4	2	0.40 ± 0.05
$[CuBr_2$(β-picoNO)$_2]_{(s)}$	Methanol	4	3	43.42 ± 2.08
$ZnBr_{2(s)}$	Methanol	11	1	-48.26 ± 0.75
β-picoNO$_{(s)}$	2:1 $ZnBr_2$–methanol	4	2	-2.17 ± 0.08
$[ZnBr_2$(β-picoNO)$_2]_{(s)}$	Methanol	4	3	28.56 ± 0.49

[a] Aqueous.

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 ($\Delta_r H^\circ$) and by using appropriate thermochemical cycles [19,27,28], 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–O bonds [15], being equal to: $\bar{D}_{(M\text{–}O)} = -\Delta_r H^\circ(g)/2$. 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 the adducts were equal to the enthalpy of sublimation of 1 mol of the ligand [31,32] 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: $NiBr_2 > CuBr_2 > CoBr_2 > ZnBr_2 > MnBr_2 > FeBr_2$. Using the $\bar{D}_{(M\text{–}O)}$ values, the order is: $MnBr_2 > FeBr_2 > CoBr_2 = NiBr_2 > ZnBr_2$. Comparing the values of $\bar{D}_{(M\text{–}O)}$ for the adducts of β-picoNO and pyNO [15] with the same stoichiometry, it is observed the basicity order: β-picoNO > pyNO, as would be expected from the inductive effect of the substitution of one hydrogen atom of the pyridine ring in pyNO by the electron donator methyl group to obtain β-picoNO. This enhances the disposal of electron density on the oxygen atom in β-picoNO relative to non-substituted pyNO.

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)	$\bar{D}_{(M\text{–}O)}$
$MnBr_{2(s)}$		-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]				
$CuBr_{2(s)}$		-141.8[a]	182.4[b]				
$ZnBr_{2(s)}$		-328.65[a]	159.7[b]				
β-picoNO$_{(s)}$		7.7 ± 0.8[c]	81.9 ± 1.5[c]				
$[MnBr_2$(β-picoNO)$_2]_{(s)}$	-76.34 ± 1.53	-443.6 ± 2.8		-454 ± 5	248.7 ± 5.0	-369 ± 4	185 ± 2
$[FeBr_2$(β-picoNO)$_2]_{(s)}$	-69.73 ± 1.31	-301.9 ± 2.8		-446 ± 5	242.1 ± 4.6	-360 ± 6	180 ± 3
$[CoBr_2$(β-picoNO)$_2]_{(s)}$	-80.97 ± 2.88	-275.5 ± 3.8		-436 ± 6	253.4 ± 5.3	-350 ± 6	175 ± 3
$[NiBr_2$(β-picoNO)$_2]_{(s)}$	-92.95 ± 1.24	-287.5 ± 2.1		-435 ± 5	265.4 ± 4.6	-349 ± 5	175 ± 3
$[CuBr_2$(β-picoNO)$_2]_{(s)}$	-82.68 ± 2.14	-206.9 ± 3.2		-437.5 ± 5.3	255.9 ± 4.9	-351.3 ± 5.5	175.7 ± 2.8
$[ZnBr_2$(β-picoNO)$_2]_{(s)}$	-72.99 ± 0.90	-390.1 ± 2.6		-411.1 ± 4.9	251.4 ± 4.9	-324.2 ± 5.4	162.1 ± 2.7

[a] [29].
[b] [15].
[c] [30].

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

Compound	$\Delta_f H^\circ$	$\Delta_r H^\circ(g)$	$\Delta_{fI} H^\circ$
$Br^-_{(g)}$	−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]		
$[MnBr_2(\beta\text{-picoNO})_2]_{(g)}$	−357 ± 6	−368 ± 4	−2631 ± 8
$[FeBr_2(\beta\text{-picoNO})_2]_{(g)}$	−216 ± 8	−360 ± 6	−2720 ± 7
$[CoBr_2(\beta\text{-picoNO})_2]_{(g)}$	−198 ± 8	−350 ± 6	−2792 ± 10
$[NiBr_2(\beta\text{-picoNO})_2]_{(g)}$	−201 ± 7	−349 ± 5	−2883 ± 9
$[CuBr_2(\beta\text{-picoNO})_2]_{(g)}$	−20.7 ± 7.4	−351.3 ± 5.54	−2927.1 ± 9.2
$[ZnBr_2(\beta\text{-picoNO})_2]_{(g)}$	−303.2 ± 7.4	−324.2 ± 5.4	−2836.1 ± 9.6

[a] [29].
[b] [33].

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

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

where

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

Table 7 lists the values obtained for these enthalpy values. Correlation of the $\Delta_{fI}H^\circ$ values with the metal atomic number is present in Fig. 1. It shows part of the double periodic variation profile of the first transition metal series. The $\Delta_{fI}H^\circ$ values obtained depends on the electronic structure of the central ion. The course of that relation allows to determine graphically the thermodynamic stabilization energy in the ligand field on the assumption that the course of variations of enthalpies of formation of the adducts is linear in a hypothetical state without influence of 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 for two bromide ions and two oxygen atoms (from two ligands) increases in the order: Fe(II) (45 kJ/mol) < Co(II) (72 kJ/mol) < Ni(II) (128 kJ/mol) < Cu(II) (129 kJ/mol). The adduct of Cu(II) bromide formed with pyNO that has the same stoichiometry of that formed by Cu(II) bromide with β-picoNO, has an stabilization energy of 107.5 kJ mol^{-1} [15]. This means that the stabilization energy provided by β-picoNO is higher than pyNO.

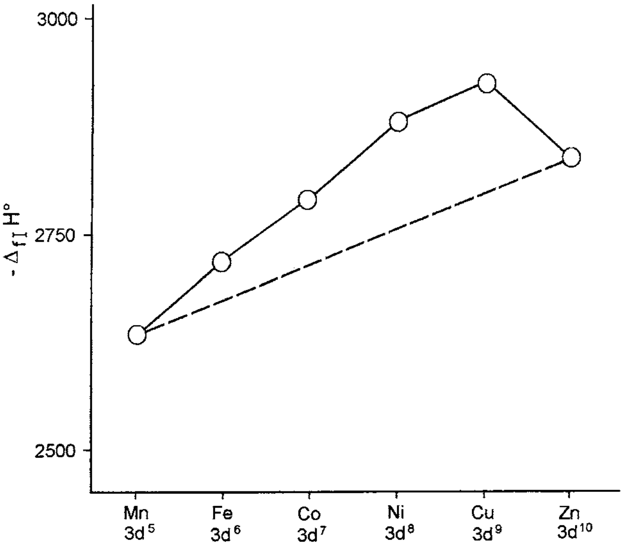

Fig. 1. Plot of enthalpy values of complex formation in the gaseous phase from ionic components against d-electron configuration.

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