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THERMOCHEMICAL PARAMETERS OF α-PICOLINE N-OXIDE ADDUCTS OF SOME DIVALENT TRANSITION METAL BROMIDES

P. O. Dunstan[*]

Instituto de Química, Universidade Estadual de Campinas, 13084-971 Campinas, São Paulo, Brazil

Thermochemical parameters for the adducts [$MBr_2(\alpha\text{-picoNO})_n$] (where M is Mn(II), Fe(II), Co(II), Ni(II), Cu(II) or Zn(II); α-picoNO is α-picoline N-oxide and n=2 or 4) were determined through reaction–solution calorimetry in methanol or aqueous 1.2 M HCl at 298 K as the standard enthalpies for the Lewis acid/base reactions, the standard enthalpies of formation, the lattice standard enthalpies, the standard enthalpies of decomposition and the standard enthalpies for the Lewis acid/base reactions in the gaseous phase. The mean bond dissociation standard enthalpies of the M(II)–oxygen coordinated bond were calculated by using the standard molar enthalpies of formation of the gaseous adducts.

Keywords: *calorimetry, enthalpy, metal(II) bromides, transition metals*

Introduction

The thermochemical data found in the literature concerning complexes of the halides of divalent elements having 3d electrons with substituted pyridine N-oxides is very poor. To obtain these data, basically thermogravimetry and differential scanning calorimetry are used [1–13].

This paper focuses on the thermochemical data for α-picoline N-oxide (α-picoNO) adducts of some bromides of divalent transition metals of the first row in the periodical table of transition elements. These results are important to determine their potential application of these metals in catalysis or in the chromatographic separation.

Experimental

The α-picoline N-oxide ligand was synthesized according to the method reported by Boekelheide *et al*. [14]. All the anhydrous salts used in the preparation of the adducts were of analytical grade.

Microanalysis (C/H/N) was carried out using a PerkinElmer elemental analyzer. The metal and bromide contents were determined by using methods found in [15, 16]. The capillary melting point temperatures for all the complexes were determined by using a Unimelt equipment of Thomas Hover Co. TG and DSC curves were recorded by means of a DuPont 951 TG analyzer, at a heating rate of 10 K min^{-1} in a dynamic argon atmosphere with a flow rate of 80 mL min^{-1}. The infrared spectra of all compounds were recorded in KBr pellets in a Perkin Elmer 1600 series FTIR spectrometer. All solution calorimetric determinations were carried out in an LKB 8700-1 isoperibolic precision calorimeter system as described before [17].

Results and discussion

According to Table 1 the C/H/N, M and Br analysis of the complexes [$MBr_2(\alpha\text{-picoNO})_n$] are in good agreement with the expected values.

The results of infrared spectroscopy for the adducts are summarized in Table 2. The ν(NO) band shifted towards lower frequencies with respect to its position in the free ligand (1254 cm^{-1}). A small decrease in the frequency of the δ(NO) band in the adducts, with respect to its position in the uncoordinated ligand (852 cm^{-1}) is observed. These facts indicate that the ligand is coordinated through its oxygen atom to the metal ions [1, 5, 18–21].

The TG curves showed mass loss after melting of most of the compounds. The mass losses took place in 2, 3, 4 or 5 steps. Some of these steps consist of two consecutive decomposition processes. They lose a part or all the ligand in the first or in the first two steps following by the loosing of the rest of the ligand, bromine and almost all their metal content in the next steps. In most cases a residue was observed, which is the respective metal [22]. Figure 1 shows the TG curve of the cobalt(II) bromide adduct. This TG curve shows three mass losses, and the corresponding DTG peaks. The first step is due to the loss of one mol ligand. The second step is due to the loss of the other

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[*] dunstan@iqm.unicamp.br

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Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

Table 1 Elemental analysis results (obs./calc. in %) for the complexes

Complex	C	N	H	*M*	Br
$[MnBr_2(\alpha\text{-picoNO})_2]$	32.98/33.29	6.33/6.47	3.29/3.26	12.65/12.69	36.89/36.91
$[FeBr_2(\alpha\text{-picoNO})_2]$	31.96/32.22	6.44/6.46	3.19/3.25	12.84/12.87	36.78/36.83
$[CoBr_2(\alpha\text{-picoNO})_2]$	32.75/32.98	6.33/6.41	3.18/3.23	13.45/13.49	36.52/36.57
$[NiBr_2(\alpha\text{-picoNO})_4]$	44.20/44.01	8.72/8.55	4.46/4.31	8.99/8.96	24.37/24.40
$[CuBr_2(\alpha\text{-picoNO})_2]$	32.89/32.64	6.37/6.34	2.99/3.20	14.44/14.39	36.19/36.21
$[ZnBr_2(\alpha\text{-picoNO})_2]$	32.71/32.50	6.33/6.32	3.02/3.18	14.78/14.74	36.05/36.04

Table 2 Main absorption bands taken from the infrared spectra (cm^{-1}) and melting points (*MP*) of the complexes

Complex	ν(N–O)	δ(N–O)	*MP*/K
$[MnBr_2(\alpha\text{-picoNO})_2]$	1208	847	432
$[FeBr_2(\alpha\text{-picoNO})_2]$	1220	849	341
$[CoBr_2(\alpha\text{-picoNO})_2]$	1198	844	432
$[NiBr_2(\alpha\text{-picoNO})_4]$	1220	849	392
$[CuBr_2(\alpha\text{-picoNO})_2]$	1204	848	407
$[ZnBr_2(\alpha\text{-picoNO})_2]$	1206	846	410

mol of ligand, following by the loss of all the bromine and part of cobalt. An 0.7 mol cobalt metal residue was obtained. It had been observed for the heating of metal(II) bromides, the loss of all the bromine and part of the metal, leads to the respective metal residue [22]. The DSC curves showed endothermic peaks due to melting and thermal decomposition of the substance accompanied by melting. Figure 2 presents the DSC curve of the $CoBr_2$ adduct. The endothermic peak is due to the melting of the adduct.

Table 3 contains the band maxima assignments and calculated ligand field parameters for the adducts [2, 3, 5, 23–25]. Most of the complexes were pseudo-tetrahedral with the metallic ion surrounded by two bromide ions and two oxygen atoms (from two ligand molecules). The nickel adduct is pseudo-octahedral with the metal ion surrounded by two bromide ions and four oxygen atoms (from four ligand molecules).

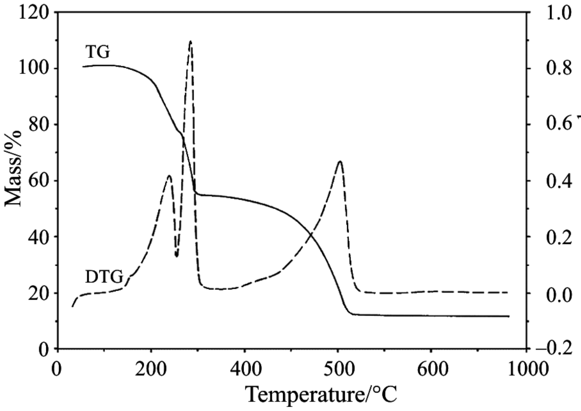

Fig. 1 TG/DTG curve of $[CoBr_2(\alpha\text{-picoNO})_2]$ complex. The residue is 0.7 mol of Co (9.53/9.44% – measured/calculated data)

$\Delta_r H_m^0$, the standard molar enthalpy of reaction was obtained from the reaction–solution enthalpies $\Delta_i H_m^0$, of each reagent and product dissolved sequentially in methanol or in 1.2 M HCl solution as it is shown in Table 4. A strict control of stoichiometry was maintained according to the general reaction [13]:

$$MBr_2(cr)+nL(cr)\rightarrow[MBr_2(L)_n](cr) \quad \Delta_r H_m^0 \qquad (1)$$

The standard molar enthalpy for each reaction was calculated from the tabulated values, applying a convenient thermochemical cycle. The thermochemical parameters obtained from the values of the

Table 3 Band maxima assignments and calculated ligand-field parameters for the complexes

Complex	Band maxima/cm^{-1}							
$[MnBr_2(\alpha\text{-picoNO})_2]$	26801							
$[CuBr_2(\alpha\text{-picoNO})_2]$	8752							
Complex	ν_1*/cm^{-1}	*Dq*/cm^{-1}						
$[FeBr_2(\alpha\text{-picoNO})_2]$	6010	601						
Complex	ν_1/cm^{-1}	ν_2/cm^{-1}	ν_4/cm^{-1}	ν_3/cm^{-1}	*Dq*/cm^{-1}	*B*/cm^{-1}	*Dq/B*	β^+
$[CoBr_2(\alpha\text{-picoNO})_2]$		6973^a		15525^b	372	756	0.492	0.779
$[NiBr_2(\alpha\text{-picoNO})_4]$	8721^c	12293^d	15834^e	21481^f	872	360	2.065	0.410

$^*\nu_1={}^5T_2\leftarrow{}^5E$; $^a\nu_2={}^4T\leftarrow{}^4A_2$; $^b\nu_3={}^4T_1(P)\leftarrow{}^4A_2$; $^c\nu_1={}^3T_{2g}\leftarrow{}^3A_{2g}$; $^d\nu_2={}^3T_{1g}(F)\leftarrow{}^3A_{2g}$; $^e\nu_4={}^1E_g\leftarrow{}^3A_{2g}$; $\beta^+=B/B_0$; $B_0=1030\ cm^{-1}$ (Ni^{2+}); $B_0=971\ cm^{-1}$ (Co^{2+}) [24].

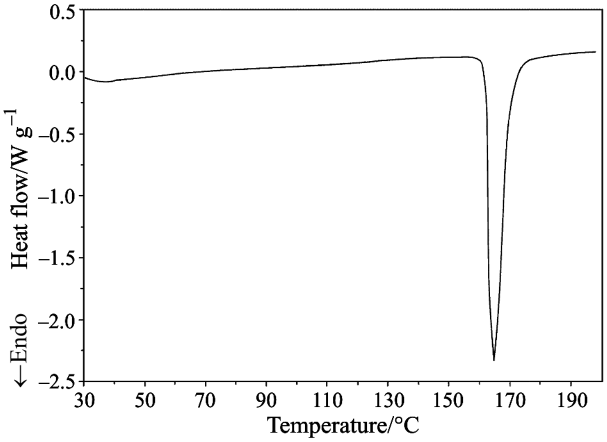

Fig. 2 DSC curve of $[CoBr_2(\alpha\text{-picoNO})_2]$ complex

standard molar enthalpies of reaction of the complexes and suitable thermochemical cycles are presented in Table 5. The auxiliary data used for the calculations are presented in Table 6.

The capillary melting points determinations and the TG and DSC curves show that the complexes decomposed on heating. So far, it was necessary to consider the sublimation enthalpies of the complexes as being equal to the sublimation enthalpy of the ligand [22], for the calculation of the standard bond dissociation enthalpy, <*D*>(M–O).

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

$$M^{2+}(g)+2Br^{-}(g)+n\alpha\text{-picoNO}(g)\rightarrow \rightarrow[MBr_2(\alpha\text{-picoNO})_n](g) \quad \Delta_{fl}H^0_m \qquad (2)$$

Table 4 Standard molar enthalpies (kJ mol^{-1}) of solution–reaction at 298 K

Reactant*	Solvent	Solution	$\Delta_i H^0_m$ /kJ mol^{-1}
$MnBr_2$(*cr*)	Methanol	A_1	–102.4±1.9
α-picoNO(*cr*)	A_1	B_1	–4.9±0.4
$[MnBr_2(\alpha\text{-picoNO})_2]$(*cr*)	Methanol	C_1	–11.4±0.4
$FeBr_2$(*cr*)	1.2 M aqueous HCl	A_2	–36.3±1.1
α-picoNO(*cr*)	A_2	B_2	–32.2±1.0
$[FeBr_2(\alpha\text{-picoNO})_2]$(*cr*)	1.2 M aqueous HCl	C_2	–18.7±0.6
$CoBr_2$(*cr*)	Methanol	A_3	–107.3±0.9
α-picoNO(*cr*)	A_3	B_3	5.0±0.2
$[CoBr_2(\alpha\text{-picoNO})_2]$(*cr*)	Methanol	C_3	–29.8±0.8
$NiBr_2$(*cr*)	1.2 M aqueous HCl	A_4	–70.5±0.5
α-picoNO(*cr*)	A_4	B_4	–62.8±1.7
$[NiBr_2(\alpha\text{-picoNO})_4]$(*cr*)	1.2 M aqueous HCl	C_4	–25.4±1.0
$CuBr_2$(*cr*)	Methanol	A_5	–37.4±0.7
α-picoNO(*cr*)	A_5	B_5	–5.2±0.2
$[CuBr_2(\alpha\text{-picoNO})_2]$(*cr*)	Methanol	C_5	55.3±1.2
$ZnBr_2$(*cr*)	Methanol	A_6	–47.7±0.7
α-picoNO(*cr*)	A_6	B_6	–5.6±0.3
$[ZnBr_2(\alpha\text{-picoNO})_2]$(*cr*)	Methanol	C_6	50.1±3.0

**cr*=crystals

Table 5 Thermochemical parameters (in kJ mol^{-1}) for the complexes

Complex	$\Delta_r H^0_m$	$\Delta_f H^0_m$	$\Delta_M H^0_m$	$\Delta_D H^0_m$	$\Delta_r H^0_m(g)$	<*D*>(M–O)
$[MnBr_2(\alpha\text{-picoNO})_2]$(*cr*)	–95.9±2.0	–463.2±3.2	–470±5	264±5	–386±6	193±3
$[FeBr_2(\alpha\text{-picoNO})_2]$(*cr*)	–49.8±1.6	–279.0±3.0	–422±5	218±5	–338±6	169±3
$[CoBr_2(\alpha\text{-picoNO})_2]$(*cr*)	–82.5±1.2	–282.8±2.9	–434±5	251±5	–350±6	175±3
$[NiBr_2(\alpha\text{-picoNO})_4]$(*cr*)	–107.9±2.0	–278.8±3.9	–615±10	445±9	–531±10	133±3
$[CuBr_2(\alpha\text{-picoNO})_2]$(*cr*)	–93.9±1.4	–294.2±2.9	–445±5	263±5	–361±5	180±3
$[ZnBr_2(\alpha\text{-picoNO})_2]$(*cr*)	–103.4±3.1	–411.5±4.0	–432±6	272±6	–347±6	174±3

Table 6 Auxiliary data for the calculations

Compound	$\Delta_f H_m^0$	$\Delta_{cr}^{g} H_m^0$	Reference	Compound	$\Delta_f H_m^0$	Reference
$MnBr_2(cr)$	–384.90	206.0	[13, 26]	$Br^-(g)$	–219.07	[26]
$FeBr_2(cr)$	–249.80	204.0	[26]	$Mn^{2+}(g)$	2522.0±0.1	[28]
$CoBr_2(cr)$	–220.90	183.0	[13, 26]	$Fe^{2+}(g)$	2751.6±2.3	[28]
$NiBr_2(cr)$	–212.10	170.0	[13, 26]	$Co^{2+}(g)$	2841.7±3.4	[28]
$CuBr_2(cr)$	–141.80	182.4	[13, 26]	$Ni^{2+}(g)$	2930.5±1.5	[28]
$ZnBr_2(cr)$	–328.65	159.7	[13, 26]	$Cu^{2+}(g)$	3054.5±2.1	[28]
α-picoNO(*cr*)	10.3±0.8	84.2±2.3	[27]	$Zn^{2+}(g)$	2781.0±0.4	[28]

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

Complex	$\Delta_f H_m^0$/kJ mol^{-1}	$\Delta_{fl} H_m^0$/kJ mol^{-1}
$[MnBr_2(\alpha\text{-picoNO})_2](g)$	–376±8	–2649±10
$[FeBr_2(\alpha\text{-picoNO})_2](g)$	–195±8	–2698±10
$[CoBr_2(\alpha\text{-picoNO})_2](g)$	–199±8	–2792±11
$[NiBr_2(\alpha\text{-picoNO})_4](g)$	–195±14	–3065±17
$[CuBr_2(\alpha\text{-picoNO})_2](g)$	–131±8	–2936±9
$[ZnBr_2(\alpha\text{-picoNO})_2](g)$	–327±8	–2859±10

where

$$\Delta_{fl} H_m^0 = \Delta_f H_m^0(\text{adducts}) - \Delta_f H_m^0(M^{2+}(g)) -$$

$$-2\Delta_f H_m^0(Br^-(g)) - n\Delta_f H_m^0(\alpha\text{-picoNO}(g))$$

Table 7 presents the obtained enthalpy values. The formation enthalpies of the adducts in gaseous phase were obtained from their respective standard enthalpies of their acid/base reactions in gaseous phase. Auxiliary data used in the calculation of $\Delta_{fl} H_m^0$ are also listed in Table 6. Correlation of these calculated values with respect to the atomic number of metal ion is presented in Fig. 3. In part it shows a double periodic variation profile of the first transition metal series.

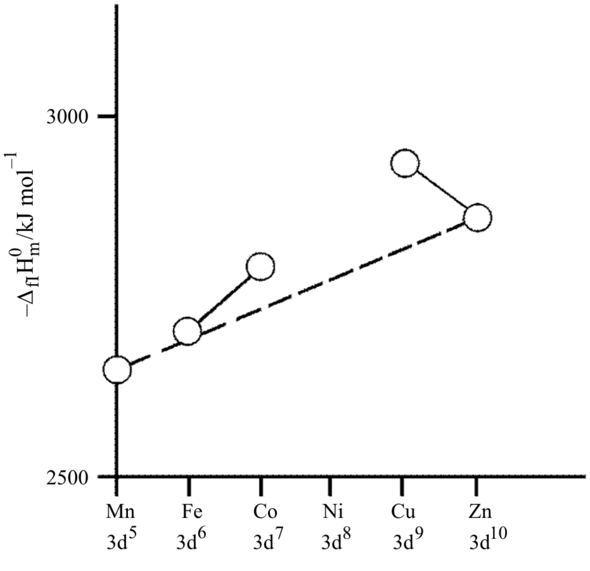

Fig. 3 Plot of enthalpy changes for complex formation in the gaseous phase from ionic components *vs*. d-electron configuration

Conclusions

Based on the <*D*>(M–O) values obtained of the complexes, the acidity order of the salts is: $MnBr_2 > CuBr_2 > CoBr_2 > ZnBr_2 > FeBr_2$. Comparing the values of <*D*>(M–O) to the adducts of pyNO [13], α-picoNO and β-picoNO [22] with the same stoichiometry, it can be observed that the basicity order of the ligands is pyNO<β-picoNO<α-picoNO. The expected order would be: α-picoNO≈β-picoNO>pyNO, due to the inductive effect of the substitution of one hydrogen atom in the pyridine ring of pyNO, by the electron donor methyl group to obtain α- or β-picoNO. It enhances the available electron density for binding over the oxygen atom in α- or β-picoNO, relative to non-substituted pyNO. This inductive effect is nearly the same in ortho- and meta-substitution. It seems that the type of bonding formed between the donor and acceptor atom is important in determining the relative strength of the interaction or another kind of interaction is acting, like intramolecular hydrogen bonding, since α-picoNO is a stronger base to these metal bromides compared to β-picoNO.

The $\Delta_{fl} H_m^0$ values obtained for the complexes vary as a function of the electronic structure of the central ion. It permits to determine graphically the EECC values, supplied by the ligand field. When the EECC of the ligand field is zero (cases of high spin d^5 Mn^{2+} and d^{10} Zn^{2+}), the course of enthalpies values must be linear [22]. In such a case, the stabilization energies are the difference between the real and the interpolated values. Thus, it was found that the EECC in the ligand field formed by two bromide ions and two oxygen atoms from two ligand molecules increases in the following order: Co(II) (52 kJ mol^{-1})<Cu(II) (115 kJ mol^{-1}). The complex formed by Co(II) with β-picoNO with the same stoichiometry [22], has an EECC of 72 kJ mol^{-1}. This means that EECC provided by two β-picoNO molecules is higher than that of two α-picoNO molecules. The complex of Cu(II) with β-picoNO with the same stoichiometry [22] has an EECC of 129 kJ mol^{-1}. This means, again that the EECC provided by two β-picoNO molecules is higher than that provided by two α-picoNO molecules.

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