Thermochemistry of Morpholine Adducts of Some Bivalent Transition Metal Bromides

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The adducts [$MBr_2(morph)_n$] (where M is Mn(II), Fe(II), Co(II), Ni(II), Cu(II), or Zn(II), morph is morpholine, and $n = 1.5$, 2, or 3) were synthesized and characterized by melting points, elemental analysis, thermal analysis, and electronic and IR spectroscopy. From calorimetric studies in solution, the standard enthalpies of formation of the adducts and several thermochemical parameters were determined. The mean standard enthalpies of the metal−nitrogen bond were calculated.

Introduction

The bidentade ligand morpholine with two donor atoms, nitrogen and oxygen, forms complexes with transition-metal halides.[1,2] However, no work seems to have been carried out on the thermodynamic properties of these compounds. The present communication describes such a study on the adducts of morpholine with the bromides of manganese(II), iron(II), cobalt(II), nickel(II), copper(II), and zinc(II). The ligand field parameters of the adducts were also calculated. The bromides were selected among several other halides because they have thermochemical data cited in the literature.[3]

Knowledge of the standard enthalpies of formation of coordination compounds is important for characterizing the compounds and for understanding their properties.[4] 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. Calorimetric measurements were made to determine the mean strength of the M−N bonds.

Experimental Section

Chemicals. Morpholine (Aldrich, > 99 %) was purified by distillation. All anhydrous metal(II) bromides used in the preparation of adducts were of reagent grade. Solvents used in the synthesis of the adducts were purified by distillation and stored over Lindle 4 Å molecular sieves.

Adducts Synthesis. The adducts were prepared by the reaction of metal(II) bromides and an excess of ligand in hot ethanol, *n*-buthanol, or *tert*-buthanol. A typical procedure is given below.

Copper(II) Bromide−Morpholine. To a solution of 0.50 g of $CuBr_2$ (2.23 mmol) in 200 cm^3 of hot ethanol, 6 cm^3 of morpholine (68.87 mmol) was slowly added dropwise with stirring. The stirring was maintained over several hours. The solid formed was filtered and washed with petroleum ether. The product was dried for several hours in a vacuum and stored in a desiccator over calcium chloride. The purity of the adducts was (99.5 to 99.9) %, as shown by chemical analysis.

Analytical Section. Carbon, hydrogen, and nitrogen were determined by microanalytical procedures.[5] Bromine analysis was made by gravimetry using standard N/10 $AgNO_3$ solution after the adducts were dissolved in water.[6]

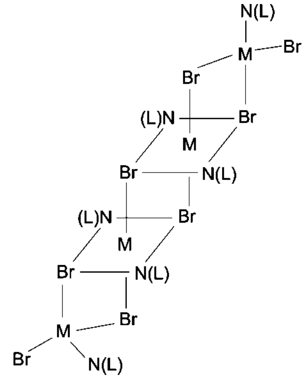

Figure 1. Structure of the polymeric compounds [MBr_2(morph)1.5].

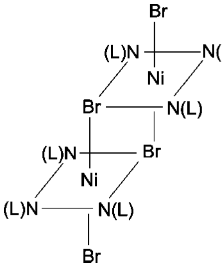

Figure 2. Structure of the polymeric compound [$NiBr_2$(morph)3].

Spectra. Infrared spectra were obtained using samples of the adducts in a KBr matrix in the region of (4000 to 400) cm^{-1} using a Perkin-Elmer 16.00 Series FTIR spectrophotometer.

Far infrared spectra were obtained using sample nulls of the adducts in nujol sandwiched between polyethylene plates in the region of (400 to 100) cm^{-1} using a Bomem FT DA8 spectrophotometer.

Thermal Studies. The TG/DTG and DSC measurements were obtained in an argon atmosphere in a DuPont 951 analyzer with samples varying in mass from (7.30 to 16.59) mg (TG/DTG) and from (3.44 to 6.07) mg (DSC) and a heating rate of 10 K·min^{-1} in the (298 to 678) K (DSC) and (298 to 1248) K (TG/DTG) temperature ranges.

Calorimetric Measurements. All solution calorimetric measurements were carried out in an LKB 8700-1 precision calorimeter, as previously described.[7] The accuracy of the calorimeter was carried out by determining the heat of dissolu-

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Table 1. Melting Points, Yields, Appearance, and Analytical Data of the Adducts

compd	yield (%)	MP (K)[a]	appearance[b]	% C calcd	% C found	% H calcd	% H found	% N calcd	% N found	% halogen calcd	% halogen found
[MnBr$_2$(morph)$_{1.5}$]	99	352	l. br. pw.	20.86	20.79	3.94	4.02	6.08	5.98	46.27	46.07
[FeBr$_2$(morph)$_{1.5}$]	62	407	br. pw.	20.81	20.63	3.93	4.01	6.07	5.97	46.14	46.16
[CoBr$_2$(morph)$_{1.5}$]	88	406	l. bl. pw.	20.62	20.40	3.89	4.03	6.01	5.98	45.74	45.75
[NiBr$_2$(morph)$_3$]	12	435	ye. pw.	30.03	29.93	5.67	5.77	8.76	8.65	33.30	33.27
[CuBr$_2$(morph)$_{1.5}$]	72	403	br. pw.	20.59	20.57	3.89	3.94	6.00	5.95	45.60	45.57
[ZnBr$_2$(morph)$_2$]	83	527	wh. pw.	24.06	24.11	4.54	4.51	7.01	7.00	40.01	39.98

[a] With decomposition. [b] Key: l., light; br., brown; bl., blue; ye., yellow; wh., white; pw., powder.

Table 2. Main IR Spectral Data[a]

compd	assignment[b] $\nu_{(N-H)}$	$\nu_{(C-C)}$	$\nu_{(C-O-C)}$	$\delta_{(N-H-C)}$	$\nu_{(M-Br)}$	$\nu_{(M-L)}$
morph	3320m, 2947s	1452s	1097s	889m, 835s		
[MnBr$_2$(morph)$_{1.5}$]	3033m	1424m	1104s	897m, 871m	276m, 258m	144s
[FeBr$_2$(morph)$_{1.5}$]	3016m	1425m	1100s	895m, 870m	275s, 259m	147m
[CoBr$_2$(morph)$_{1.5}$]	3016m	1425m	1104s	896m, 871s	276m, 259m	149s
[NiBr$_2$(morph)$_3$]	3016m, 2949m	1425m	1100s	895m, 870s	276m, 258m	148s
[CuBr$_2$(morph)$_{1.5}$]	3016m	1425m	1104s	896m, 871s	154s	
[ZnBr$_2$(morph)$_2$]	3201m, 3136m	1444m	1116s	878s	247s, 223s	318s

[a] Intensity of bands: s, strong; m, medium. [b] Key: ν, stretching; δ, angular deformation.

Table 3. Thermoanalytical Data of the Compounds

compd	apparent melting point (K)	weight loss (%) calcd	weight loss (%) obsd	TG temperature range (K)	species lost	DSC temperature peak temperature (K)	ΔH^θ (kJ·mol^{-1})
[MnBr$_2$(morph)$_{1.5}$]	352	26.09	26.72	392 to 588	−0.75 L	429	8.84
		12.17	11.09	588 to 641	−0.35 L	450	8.81
		48.61	50.29	936 to 1032	−0.4 L, −1.5 Br	505	10.13
			11.90[a]				
[FeBr$_2$(morph)$_{1.5}$]	407	25.16	26.76	410 to 525	−L	424	22.24
		12.58	12.65	525 to 565	−0.5 L	468	31.31
		34.61	37.97	836 to 1039	−1.5 Br		
			22.62[a]				
[CoBr$_2$(morph)$_{1.5}$]	406	12.46	11.89	364 to 405	−0.5 L	379	26.86
		24.93	21.13	405 to 546	−L	456	−85.12
		11.44	11.95	546 to 635	−0.5 Br		
		37.68	41.74	635 to 953	−1.5 Br, −0.2 Co		
			13.39[a]				
[NiBr$_2$(morph)$_3$]	435	12.10	12.12	412 to 466	−0.66 L	463	88.73
		63.19	63.90	466 to 596	−2.33 L, −1.25 Br		
		18.60	18.94	596 to 966	−0.75 Br, −0.5 Ni		
			4.98[a]				
[CuBr$_2$(morph)$_{1.5}$]	403	19.09	17.67	367 to 390	−0.75 L	346	1.52
		36.21	33.43	390 to 626	−0.75 L, −0.75 Br	398	−101.09
		37.62	38.14	626 to 876	−1.25 Br, −0.5 Cu		
			8.33[a]				
[ZnBr$_2$(morph)$_2$]	527	37.08	37.46	469 to 533	−1.7 L	538	57.92
		56.37	55.27	533 to 741	−0.3 L, −2 Br, −0.6 Zn		
		4.91	5.31	741 to 1038	−0.3 Zn		
			1.96[a]				

[a] Residue at 1243 K.

Table 4. Band Maxima and Calculated Ligand Field Parameters for the Compounds[a]

compd	band maxima (·10^3 cm^{-1}) d-d	interligand + charge transfer
[MnBr$_2$(morph)$_{1.5}$]	11.9	28.6

compd	band maxima (·10^3 cm^{-1}) d-d ν_1[b]		Dq (cm^{-1})	interligand + charge transfer
[FeBr$_2$(morph)$_{1.5}$]	10.6	1063		29.2

compd	band maxima (·10^3 cm^{-1}) d-d ν_1	ν_2	ν_4	ν_3	Dq (cm^{-1})	B (cm^{-1})	Dq/B	β^+	interligand + charge transfer
[CoBr$_2$(morph)$_{1.5}$]	8.66[c]	16.7[c]		20.5[c]	806	974	0.827	1.003	38.8
		6.41[c]		15.9[d]	356	772	0.461	0.795	
[NiBr$_2$(morph)$_3$]	7.24[e]	12.3[e]	15.2[e]	23.4[e]	724	976	0.741	0.948	31.5

compd	band maxima (·10^{3}cm^{-1}) d-d
[CuBr$_2$(morph)$_{1.5}$]	13.0

[a] $\beta^+ = B/B_0$; $B_0 = 971$ cm^{-1} (Co^{2+})[19]; $B_0 = 1030$ cm^{-1} (Ni^{2+})[19]. [b] $\nu_1 = {}^5E_g \leftarrow {}^5T_{2g}$. [c] $\nu_1 = {}^4T_{2g} \leftarrow {}^4T_{1g}(F)$; $\nu_2 = {}^4A_{2g} \leftarrow {}^4T_{1g}(F)$; $\nu_3 = {}^2P, {}^2G, {}^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$. [d] $\nu = {}^4T_1(F) \leftarrow {}^4A_2$; $\nu_3 = {}^4T_1(P) \leftarrow {}^4A_{2g}$. [e] $\nu_1 = {}^3T_{2g} \leftarrow {}^3A_{2g}$; $\nu_2 = {}^3T_{1g}(F) \leftarrow {}^3A_{2g}$; $\nu_4 = {}^1E_g \leftarrow {}^3A_{2g}$; $\nu_3 = {}^3T_{1\ g}(P) \leftarrow {}^3A_{2g}$.

Table 5. Enthalpies of Dissolution at 298.15 K

$\mathrm{MnBr}_{2(s)} + 1.2\ \mathrm{M\ HCl}$

m/mg	$n \cdot 10^5$/mol	Q_r/J
15.8	7.36	−4.51
27.2	12.7	−6.27
32.2	15.0	−8.22
38.8	18.1	−10.61
59.3	27.6	−15.82

$\Delta_1 H^\theta/\mathrm{kJ \cdot mol^{-1}} = -56.55 \pm 1.39$

$1.5\ \mathrm{morph}_{(l)} + \mathrm{MnBr}_2 - 1.2\ \mathrm{M\ HCl}$

m/mg	$n \cdot 10^5$/mol	Q_r/J
6.41	7.36	−4.40
15.7	18.0	−10.48
27.2	12.7	−11.55
32.2	15.0	−12.85

$\Delta_2 H^\theta/\mathrm{kJ \cdot mol^{-1}} = -89.59 \pm 2.09$

$[\mathrm{MnBr}_2(\mathrm{morph})_{1.5}]_{(s)} + 1.2\ \mathrm{M\ HCl}$

m/mg	$n \cdot 10^6$/mol	Q_r/J
3.2	9.26	−0.05043
18.9	54.7	−0.23054
23.6	68.3	−0.32275
27.3	79.0	−0.35971
28.6	82.8	−0.35971

$\Delta_3 H^\theta/\mathrm{kJ \cdot mol^{-1}} = -4.48 \pm 0.09$

$\mathrm{FeBr}_{2(s)} + 1.2\ \mathrm{M\ HCl}$

m/mg	$n \cdot 10^5$/mol	Q_r/J
14.5	6.72	−2.49
24.5	11.4	−4.40
23.8	11.0	−4.28
15.4	7.14	−2.60
40.8	18.9	−7.40
25.5	11.8	−4.30
12.8	5.94	−2.46

$\Delta_1 H^\theta/\mathrm{kJ \cdot mol^{-1}} = -38.42 \pm 0.57$

$1.5\ \mathrm{morph}_{(l)} + \mathrm{FeBr}_2 - 1.2\ \mathrm{M\ HCl}$

m/mg	$n \cdot 10^5$/mol	Q_r/J
11.4	13.09	−8.05
25.7	29.50	−18.11
16.7	19.17	−11.93
12.0	13.77	−3.97
22.3	25.60	−15.63

$\Delta_2 H^\theta/\mathrm{kJ \cdot mol^{-1}} = -94.58 \pm 5.61$

$[\mathrm{FeBr}_2(\mathrm{morph})_{1.5}]_{(s)} + 1.2\ \mathrm{M\ HCl}$

m/mg	$n \cdot 10^6$/mol	Q_r/J
11.2	32.34	−0.61
17.0	49.08	−1.07
21.2	61.21	−1.35
30.7	88.63	−2.01

$\Delta_3 H^\theta/\mathrm{kJ \cdot mol^{-1}} = -22.12 \pm 0.77$

$\mathrm{CoBr}_{2(s)} + 1.2\ \mathrm{M\ HCl}$

m/mg	$n \cdot 10^5$/mol	Q_r/J
21.8	9.966	−6.96
31.9	14.58	−10.62
53.4	24.41	−17.82
12.9	5.897	−4.26
42.3	19.34	−14.07
51.2	23.41	−17.16

$\Delta_1 H^\theta/\mathrm{kJ \cdot mol^{-1}} = -72.84 \pm 0.33$

$1.5\ \mathrm{morph}_{(l)} + \mathrm{CoBr}_2 - 1.2\ \mathrm{M\ HCl}$

m/mg	$n \cdot 10^5$/mol	Q_r/J
8.1	9.297	−5.08
28.3	32.48	−18.83
12.1	13.89	−7.92
28.7	32.94	−19.48

$\Delta_2 H^\theta/\mathrm{kJ \cdot mol^{-1}} = -80.23 \pm 0.60$

$[\mathrm{CoBr}_2(\mathrm{morph})_{1.5}]_{(s)} + 1.2\ \mathrm{M\ HCl}$

m/mg	$n \cdot 10^6$/mol	Q_r/J
10.5	30.04	−1.48
23.3	66.68	−3.39
28.3	80.98	−4.14
40.1	11.48	−5.82

$\Delta_3 H^\theta/\mathrm{kJ \cdot mol^{-1}} = -50.79 \pm 0.18$

$\mathrm{NiBr}_{2(s)} + 1.2\ \mathrm{M\ HCl}$

m/mg	$n \cdot 10^6$/mol	Q_r/J
40.5	185.3	−13.38
30.8	140.9	−10.72
57.6	263.6	−19.88
25.8	118.0	−8.58
21.5	98.38	−7.22
3.30	15.10	−1.01
7.90	36.15	−2.48
27.3	124.9	−8.83
46.5	212.8	−14.91
12.4	56.74	−3.94
25.1	114.9	−8.14
36.4	166.6	−11.28

$\Delta_1 H^\theta/\mathrm{kJ \cdot mol^{-1}} = -72.50 \pm 0.69$

$3\ \mathrm{morph}_{(l)} + \mathrm{NiBr}_2 - 1.2\ \mathrm{M\ HCl}$

m/mg	$n \cdot 10^6$/mol	Q_r/J
14.4	165.3	−10.34
30.4	348.9	−22.45
36.4	166.6	−32.77
34.0	390.3	−24.95

$\Delta_2 H^\theta/\mathrm{kJ \cdot mol^{-1}} = -196.47 \pm 2.16$

$[\mathrm{NiBr}_2(\mathrm{morph})_3]_{(s)} + 1.2\ \mathrm{M\ HCl}$

m/mg	$n \cdot 10^6$/mol	Q_r/J
5.3	11.13	0.30
12.4	26.04	0.85
11.7	24.57	0.75
16.7	35.07	1.03

$\Delta_3 H^\theta/\mathrm{kJ \cdot mol^{-1}} = 30.35 \pm 0.86$

$\mathrm{CuBr}_{2(s)} + 1.2\ \mathrm{M\ HCl}$

m/mg	$n \cdot 10^5$/mol	Q_r/J
32.7	14.64	−4.09
59.5	26.64	−7.54
30.8	13.79	−3.61
73.4	32.86	−8.35

$\Delta_1 H^\theta/\mathrm{kJ \cdot mol^{-1}} = -26.65 \pm 0.93$

$1.5\ \mathrm{morph}_{(l)} + \mathrm{CuBr}_2 - 1.2\ \mathrm{M\ HCl}$

m/mg	$n \cdot 10^5$/mol	$\mathrm{Q_{r/J}}$
13.5	15.49	−8.26
22.1	14.64	−13.93
36.7	42.12	−24.08
20.9	23.99	−12.88
24.4	28.01	−16.02
46.9	53.83	−29.81

$\Delta_2 H^\theta/\mathrm{kJ \cdot mol^{-1}} = -90.66 \pm 0.88$

$[\mathrm{CuBr}_2(\mathrm{morph})_{1.5}]_{(s)} + 1.2\ \mathrm{M\ HCl}$

m/mg	$n \cdot 10^5$/mol	Q_r/J
7.4	2.11	−0.68
11.8	3.37	−0.96
18.1	5.17	−1.68
13.5	3.86	−1.16

$\Delta_3 H^\theta/\mathrm{kJ \cdot mol^{-1}} = -31.12 \pm 0.93$

$\mathrm{ZnBr}_{2(s)}$ + Methanol

m/mg	$n \cdot 10^5$/mol	Q_r/J
25.8	11.46	−5.93
23.5	10.43	−4.83
19.4	8.62	−3.97
16.6	22.74	−11.47
55.6	24.69	−12.08
56.2	24.96	−12.94
75.2	33.39	−16.05
75.3	33.44	−17.12

$\Delta_1 H^\theta/\mathrm{kJ \cdot mol^{-1}} = -49.87 \pm 0.63$

$2\ \mathrm{morph}_{(l)} + \mathrm{ZnBr}_2$ −Methanol

m/mg	$n \cdot 10^5$/mol	Q_r/J
53.5	61.41	−8.55
35.6	40.86	−5.42
20.7	23.76	−3.69
56.3	64.62	−9.42
39.1	44.88	−5.11

$\Delta_2 H^\theta/\mathrm{kJ \cdot mol^{-1}} = -25.46 \pm 1.31$

$[\mathrm{ZnBr}_2(\mathrm{morph})_2]_{(s)}$ + Methanol

m/mg	$n \cdot 10^5$/mol	Q_r/J
7.0	1.75	−0.77
15.2	3.81	−1.57
17.8	4.46	−2.30
30.9	7.74	−3.67
23.4	5.86	−2.63

$\Delta_3 H^\theta/\mathrm{kJ \cdot mol^{-1}} = -46.71 \pm 1.43$

Table 6. Summary of the Thermochemical Results ($kJ \cdot mol^{-1}$) for Metal(II) Bromides and Their Adducts

compd	$\Delta_r H^\theta$	$\Delta_f H^\theta$	$\Delta_{s,l}{}^{g} H^\theta$	$\Delta_M H^\theta$	$\Delta_D H^\theta$	$\Delta_r H^\theta(g)$	$\bar{D}_{(M\text{-}N)}$
$MnBr_{2(s)}$		−384.9[23]	206[23]				
$FeBr_{2(s)}$		−249.8[23]	204[23]				
$CoBr_{2(s)}$		−220.9[23]	183[23]				
$NiBr_{2(s)}$		−212.1[23]	170[23]				
$CuBr_{2(s)}$		−141.8[23]	182.4[23]				
$ZnBr_{2(s)}$		−328.65[23]	159.7[23]				
$Morph_{(l)}$		−170.2[24]	42.3[24]				
$[MnBr_2(morph)_{1.5}]_{(s)}$	−141.66 ± 2.51	−781.9 ± 3.5	42.3 ± 9.0[25]	−411.0 ± 3.5	205.1 ± 2.9	−368.7 ± 9.7	245.8 ± 4.8
$[FeBr_2(morph)_{1.5}]_{(s)}$	−110.88 ± 5.69	−616.0 ± 6.2	42.3 ± 9.0[25]	−378 ± 6	174.3 ± 5.9	−336 ± 11	224 ± 7
$[CoBr_2(morph)_{1.5}]_{(s)}$	−102.28 ± 0.71	−578.5 ± 2.6	42.3 ± 9.0[25]	−349 ± 3	165.7 ± 1.6	−306 ± 9	204 ± 6
$[NiBr_2(morph)_3]_{(s)}$	−299.32 ± 2.43	−1022.0 ± 4.0	42.3 ± 9.0[25]	−596 ± 4	426.2 ± 3.9	−554 ± 10	185 ± 3
$[CuBr_2(morph)_{1.5}]_{(s)}$	−86.19 ± 1.58	−562.4 ± 3.0	42.3 ± 9.0[25]	−332.0 ± 3.0	149.6 ± 2.2	−289.7 ± 9.3	193.1 ± 6.2
$[ZnBr_2(morph)_2]_{(s)}$	−28.62 ± 2.04	−697.7 ± 3.5	42.3 ± 9.0[25]	−273 ± 4	113.2 ± 2.9	−254 ± 10	115 ± 5

tion of tris(hydroxymethylamino) methane in 0.1 $mol \cdot dm^{-3}$ hydrochloric acid. The result, (−29.78 ± 0.03) $kJ \cdot mol^{-1}$ is in agreement with the value recommended by IUPAC, (−29.763 ± 0.003) $kJ \cdot mol^{-1}$.[8] The uncertainty intervals are twice the standard deviations of the means of about 4 to 12 replicate measurements on each compound.

Results and Discussion

All adducts were solids. The yields range from (12 to 99) %. The yields, capillary melting points, colors, appearance and analytical data are summarized in Table 1.

Infrared Spectra. The pattern of the infrared spectra of the adducts is similar to that of the free ligand, although dislocation and splitting of some bands is observed. No bands due to the presence of water were observed. Considerable shifts to lower frequencies of the N−H stretching modes of the coordinated morpholine are observed. This indicates the coordination of the ligand to the metallic ion.[9−12] The positive shift of the C−O−C stretching vibration that is found at 1097 cm^{-1} in the free ligand excludes the possibility of oxygen-to-metallic ion coordination.[10] In the H−N−C deformation region, a great change is observed that affords evidence of the coordination of the N atom of the ligand.[13,14] The metal−nitrogen and metal−bromide stretching modes in the low frequency IR region are assigned.[1,15,16] Table 2 presents the extracted infrared spectral data of the adducts.

Thermal Studies. The thermogravimetry of the adducts shows the loss of the ligand in several steps of mass loss followed by the loss of bromine together or in another step of mass loss. All adducts left a residue that is part of the metal content. The DSC curves are consistent with the TG data. They present endothermic peaks because of the elimination of the ligand and exothermic peaks as a result of the redox decomposition of the intermediate compounds. Table 3 presents the thermoanalytical data of the adducts.

Electronic Spectra. Table 4 contains the band maxima assignments and calculated ligand parameters for the adducts.[16−22] The adducts of Mn(II), Fe(II), Co(II), and Cu(II) are pseudo-octahedral with two nitrogen atoms from two ligand molecules and four bromide ions surrounding each metal ion in a polymeric structure of bridging bromide ions[20] (Figure 1). The adduct of Ni(II) is pseudo-octahedral with three nitrogen atoms from three ligand molecules and three bromide ions surrounding each nickel ion in a dimeric structure of bridging bromide ions[17−19] (Figure 2).

Calorimetric Measurements. The standard enthalpies of dissolution of metal(II) bromides, morpholine, and adducts were obtained as previously reported.[6] The standard enthalpies of dissolution were obtained according to the standard enthalpies of the following reactions in solution

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

$$n\ \text{morph}_{(l)} + \text{solution A} \rightarrow \text{solution B}; \quad \Delta_2 H^\theta \qquad (2)$$

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

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

The application of the Hess law to the series of reactions 1, 2, 3, and 4 gives the standard enthalpies ($\Delta_r H^\theta$) according to the reaction

$$MBr_{2(s)} + n\ \text{morph}_{(l)} \rightarrow [MBr_2(\text{morph})_n]_{(s)}; \quad \Delta_r H^\theta \qquad (5)$$

where $\Delta_r H^\theta = \Delta_1 H^\theta + \Delta_2 H^\theta - \Delta_3 H^\theta$ because the final thermodynamic state of reactions 2and 3 are the same and $\Delta_4 H^\theta = 0$, as is also experimentally observed for the dilution of solution B in solution C. Table 5 gives the values obtained for the enthalpies of dissolution of MBr_2 ($\Delta_1 H^\theta$), morpholine in the solution of MBr_2 ($\Delta_2 H^\theta$), and the adducts ($\Delta_3 H^\theta$). Uncertainty intervals given in this table are twice the standard deviation of the means of 4 to 12 replicate measurements. Electronic spectra revealed that all adducts (except, probably, the Zn(II) adduct) exist as polymers in the solid state with bridges of bromide ions linking the metallic ions.[20] The thermochemical parameters for them were calculated per mole of $[MBr_2(\text{morph})_n]$ unit.

From the values obtained for the standard enthalpies of reaction 5 ($\Delta_r H^\theta$) and by using appropriate thermochemical cycles,[7] 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 reaction in the gaseous phase ($\Delta_r H^\theta(g)$). The standard enthalpies of the metal(II)−nitrogen bonds are equal to: $\bar{D}_{(M-N)} = (\Delta_r H^\theta(g)/n)$.[7] Table 6 lists the values obtained for these enthalpies. On the basis of the $\Delta_r H^\theta$ or the $\bar{D}_{(M-N)}$ values for the adducts, the acidity order of the salts can be established: $MnBr_2 > FeBr_2 > CoBr_2 > CuBr_2$.

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