Thermochemistry of 4-Cyanopyridine Adducts of Some Bivalent Transition Bromides

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The adducts [$MBr_2(4\text{-cyanopy})_n$] (where M is Mn(II), Fe(II), Co(II), Ni(II), Cu(II), or Zn(II); 4-cyanopy is 4-cyanopyridine; $n = 1$ or 2) were synthesized and characterized by melting points, elemental analysis, thermal analysis, 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 bonds were calculated.

Introduction

The standard enthalpies of formation of coordination compounds are important for their characterization and for understanding their properties.[1] Thermochemical parameters related to transition metal−nitrogen coordinated bonds are limited. Also, the ligand 4-cyanopyridine is known to form coordination compounds with ions of transition metals.[2–6] It has two nitrogen atoms that are potential donor atoms.

The present communication describes a study on the adducts formed by 4-cyanopyridine with the bromides of manganese(II), iron(II), cobalt(II), nickel(II), copper(II), and zinc(II). Knowledge of the thermodynamic properties of these complexes is important to determine their potential applications in catalysis or in the chromatographic separation of ionic metals.

Experimental Section

Materials. 4-Cyanopyridine (p.a. Baker) was purified by recrystallation from ethanol. All of the 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 Linde 4 Å molecular sieves.

Methods. The adducts were prepared by the reaction of the metal(II) bromides and 4-cyanopyridine in hot ethanol, with a molar ratio of 1:2. A typical procedure is given below.

The procedure for the cobalt bromide adduct is as follows. To a solution of 1.00 g of $CoBr_2$ (4.57 mmol) in 30 cm^3 of boiling ethanol (78 °C), 0.95 g of 4-cyanopyridine in 30 cm^3 of boiling ethanol was added slowly and dropwise with stirring. The stirring was maintained over several hours. The solid formed was filtered and washed with three portions of 20 cm^3 of 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 (99.4 to 99.8) % as shown by elemental analysis of C, H, N, Br, and metal contents.

Carbon, hydrogen, and nitrogen contents were determined by microanalytical procedures.[7] Bromine analysis was made by gravimetry using standard N/10 $AgNO_3$ solution, after the adducts were dissolved in water.[8] Metal contents were determined by complexometric titration with 0.01 M ethylenediaminetetraacetic acid solution of the aqueous solution of the adducts.[9]

Apparatus. IR 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 1600 series Fourier transform IR spectrophotometer.

Thermogravimetric or differential thermogravimetric (TG/DTG) and differential scanning calorimetry (DSC) measurements were obtained in an argon atmosphere in a DuPont 951 analyzer, with samples varying in mass from (3.21 to 12.04) mg (TG/DTG) and from (1.97 to 4.55) mg (DSC) and a heating rate of 10 $K\cdot min^{-1}$ in the (298 to 678) K (DSC) and (298 to 1248) K (TG/DTG) temperature ranges.

All of the solution calorimetric measurements were carried out in a LKB 8700-1 precision calorimeter. Each measurement was performed at 298.15 ± 0.02 K with a thin-walled ampule-containing reactant which was broken in a 100 mL glass reaction vessel containing 100.00 mL of calorimetric solvent.[9] The accuracy of the calorimeter was carried out by determining the heat of dissolution of tris(hydroxy-methylamino) 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) $kJ\cdot mol^{-1}$.[10] The uncertainty intervals are twice the standard deviations of the means of about three to six replicate measurements on each compound.

Results and Discussion

All of the adducts were solids. The yields ranged from (34 to 88) %. The yields, capillary melting points, colors, appearance, and analytical data are summarized in Table 1.

Infrared Spectra. The more important IR bands are reported in Table 2. Shifts to higher frequencies of the band observed at (1216 cm^{-1}) in the free ligand are observed in the adducts. The band attributed to the stretching of the nitrile group in the free ligand (2236 cm^{-1}) increases very little in frequency but dramatically decreases in intensity after coordination. These exclude the coordination of 4-cyanopyridine through the nitrogen atom of the nitrile group.[11,12] The IR spectra of the adducts can be interpreted in terms of coordination of the ligand through the heterocyclic nitrogen atom to the metal(II) ions.

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. Some metal content is lost together with bromine in the last step of mass loss. All of the adducts left a residue that is part

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

	yield	MP[a]		% C		% H		% N		% Br		% M	
compound	%	K	appearance[b]	calcd	found	calcd	found	calcd	found	calcd	found	calcd	found
$[MBr_2(4\text{-cyanopy})_2]$	46	475−7	wh. pw.	34.08	34.23	1.91	2.06	13.25	13.02	37.78	37.89	12.99	13.03
$[FeBr_2(4\text{-cyanopy})]$	38	411−3	l. or. pw.	22.37	22.50	1.26	1.33	8.76	8.86	49.98	49.73	12.46	12.35
$[CoBr_2(4\text{-cyanopy})]$	67	523−5	l. pu. pw.	33.76	33.56	1.89	1.89	13.12	12.99	37.43	37.50	13.80	13.95
$[NiBr_2(4\text{-cyanopy})_2]$	51	483−5	ye. pw.	33.77	33.41	1.89	1.73	13.13	12.97	37.45	37.53	13.76	13.81
$[CuBr_2(4\text{-cyanopy})_2]$	88	515−7	l. gre. pw.	33.36	33.31	1.87	1.79	12.97	12.83	36.99	37.18	14.70	14.87
$[ZnBr_2(4\text{-cyanopy})_2]$	57	502−3	wh. pw.	33.26	33.15	1.86	1.91	12.93	12.84	36.87	36.65	15.08	14.98

[a] Melting point with decomposition. [b] Key: l., light; wh., white; or., orange; pu., purple; ye., yellow; gre., green; pw., powder.

Table 2. Main IR Spectral Data (cm^{-1}) of the Compounds

	assignment[a]		
compound	$\nu_{(C-N)}$[b]	ring	$\nu_{(C-C)}$
4-cyanopy	2236, s	1216, s	1594, vs; 1545, vs
$[MnBr_2(4\text{-cyanopy})_2]$	2241, m	1212, m	1606, vs
$[FeBr_2(4\text{-cyanopy})]$	2236, w	1220, m	1603, vs
$[CoBr_2(4\text{-cyanopy})_2]$	2234, w	1218, m	1607, vs
$[NiBr_2(4\text{-cyanopy})_2]$	2235, m	1212, m	1608, s
$[CuBr_2(4\text{-cyanopy})_2]$	2242, w	1219, m	1612, s
$[ZnBr_2(4\text{-cyanopy})_2]$	2240, w	1224, m	1615, vs

[a] Key: ν, stretching; ring, ring breathing. [b] Intensity of bands: vs, very strong; s, strong; m, medium; w, weak.

of the metal content. The DSC curves are consistent with the TG data. They present endothermic peaks due to the elimination of ligand and exothermic peaks due to the redox decomposition of the intermediate compounds. Table 3 presents the thermoanalytical data of the adducts.

Calorimetric Measurements. The standard enthalpies of dissolution of metal(II) bromides, 4-cyanopyridine, and adducts were obtained as previously reported.[13] The standard enthalpies of dissolution were obtained according to the standard enthalpies of the following reactions in solution:

$$MBr_{2(s)} + \text{calorimetric solvent} \rightarrow \text{solution A} \qquad \Delta_1H^\theta \quad (1)$$

$$n(\text{4-cyanopy}_{(s)}) + \text{solution A} \rightarrow \text{solution B} \qquad \Delta_2H^\theta \quad (2)$$

$$[MBr_2(\text{4-cyanopy})_n]_{(s)} + \text{calorimetric solvent} \rightarrow \text{solution C} \qquad \Delta_3H^\theta \quad (3)$$

$$\text{solution B} \rightarrow \text{solution C} \qquad \Delta_4H^\theta \quad (4)$$

The application of the Hess's law to the series of reactions 1 to 4 gives the standard enthalpies of reaction (Δ_rH^θ) according to the reaction:

$$MBr_{2(s)} + n(\text{4-cyanopy})_{(s)} \rightarrow [MBr_2(\text{4-cyanopy})_n]_{(s)} \qquad \Delta_rH^\theta \quad (5)$$

where $\Delta_rH^\theta = \Delta_1H^\theta + \Delta_2H^\theta - \Delta_3H^\theta$ since the final state of reactions 2 and 3 is the same and $\Delta_4H^\theta = 0$, as was observed experimentally for the dilution of solution B into solution C. Table 4 gives the values obtained for the enthalpies of dissolution of MBr_2 (Δ_1H^θ) and 4-cyanopy into the solution of MBr_2 (Δ_2H^θ) and of the adducts (Δ_3H^θ). Uncertainty intervals given in this table are twice the standard deviation of the means of three to six replicate measurements.

From the values obtained for the standard enthalpies of reaction 5 (Δ_rH^θ) and by using appropriate thermochemical cycles,[13] the following thermochemical parameters for the

Table 3. Thermoanalytical Data of the Compounds

compound	apparent melting point (K)	weight loss (%) calcd	weight loss (%) obs	TG temperature range (K)	species lost	DSC peak temperature (K)	ΔH^θ $kJ \cdot mol^{-1}$
$[MnBr_2(4\text{-cyanopy})_2]$	475−7	7.88	8.16	348 to 370	−0.32 L	376	128.59
		20.68	22.75	445 to 486	−0.84 L	533	110.07
		20.68	22.66	486 to 560	−0.84 L		
		40.38	38.43	943 to 1026	−2 Br, −0.4 Mn		
			8.00[a]				
$[FeBr_2(4\text{-cyanopy})]$	411−3	21.59	21.53	357 to 429	−0.66 L	357	15.18
		35.79	34.90	429 to 605	−0.34 L, −Br	411	−31.05
		27.61	30.00	605 to 897	−Br, −0.15 Fe	521	3.40
			15.00[a]				
$[CoBr_2(4\text{-cyanopy})_2]$	523−5	24.39	23.50	442 to 471	−L	546	68.27
		24.39	21.44	471 to 655	−L		
		1.87	2.80	655 to 615	−0.1 Br		
		31.82	35.13	841 to 925	−1.7 Br		
			17.13[a]				
$[NiBr_2(4\text{-cyanopy})_2]$	483−5	24.40	24.78	475 to 505	−L	359	6.87
		24.40	24.70	505 to 584	−L	556	75.32
		33.71	34.61	859 to 957	−1.8 Br		
			17.00[a]				
$[CuBr_2(4\text{-cyanopy})_2]$	515−7	57.45	58.52	438 to 477	−2 L, −0.5 Br	504	66.93
		34.36	33.26	749 to 842	−1.5 Br, −0.45 Cu	528	−153.92
			8.00[a]				
$[ZnBr_2(4\text{-cyanopy})_2]$	502−3	20.42	20.52	446 to 479	−0.85 L	502	43.99
		8.41	8.77	479 to 681	−0.35 L	546	−6.15
		62.12	61.07	681 to 823	−0.80 L, −2 Br, −0.4 Zn		
		4.52	5.01	823 to 1041	−0.3 Zn		
			4.60[a]				

[a] Residue at 1253 K.

Table 4. Enthalpies of Dissolution at 298.15 K

compound	calorimetric solvent	number of experiments	$\Delta_i H^\theta$ ($kJ \cdot mol^{-1}$)
$MnBr_{2(s)}$	HCl, 1.2 M	5	-43.38 ± 0.93
4-cyanopy$_{(s)}$	2:1 $MnBr_2$−HCl, 1.2 M	3	16.61 ± 0.43
$[MnBr_2(4\text{-cyanopy})_2]_{(s)}$	HCl, 1.2 M	4	16.86 ± 0.98
$FeBr_{2(s)}$	HCl, 1.2 M	3	-37.38 ± 1.11
cyanopy$_{(s)}$	1;1 $FeBr_2$−HCl, 1.2 M	5	7.07 ± 0.17
$[FeBr_2(4\text{-cyanopy})]$	HCl, 1.2 M	3	-5.24 ± 0.09
$CoBr_{2(s)}$	HCl, 1.2 M	6	-66.87 ± 0.87
4-cyanopy$_{(s)}$	2:1 $CoBr_2$−HCl, 1.2 M	3	13.24 ± 0.26
$[CoBr_2(4\text{-cyanopy})_2]_{(s)}$	HCl, 1.2 M	3	15.63 ± 0.59
$NiBr_{2(s)}$	HCl, 1.2 M	3	-61.42 ± 0.60
4-cyanopy$_{(s)}$	2:1 $NiBr_2$−HCl, 1.2 M	5	11.04 ± 0.74
$[NiBr_2(4\text{-cyanopy})_2]_{(s)}$	HCl, 1.2 M	4	2.62 ± 0.13
$CuBr_{2(s)}$	HCl, 1.2 M	6	-26.95 ± 0.59
4-cyanopy$_{(s)}$	2:1 $CuBr_2$−HCl, 1.2 M	5	11.60 ± 0.63
$[CuBr_2(4\text{-cyanopy})_2]_{(s)}$	HCl, 1.2 M	6	24.13 ± 0.58
$ZnBr_{2(s)}$	HCl, 1.2 M	5	-41.89 ± 2.58
4-cyanopy$_{(s)}$	2:1 $ZnBr_2$−HCl, 1.2 M	5	11.81 ± 0.44
$[ZnBr_2(4\text{-cyanopy})_2]_{(s)}$	HCl, 1.2 M	5	23.32 ± 0.44

Table 5. Summary of the Thermochemical Results ($kJ \cdot mol^{-1}$) for Metal Bromides and Their 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[14]	206[14]				
$FeBr_{2(s)}$		-249.8[14]	204[14]				
$CoBr_{2(s)}$		-220.9[14]	183[14]				
$NiBr_{2(s)}$		-212.1[14]	170[14]				
$CuBr_{2(s)}$		-141.8[14]	182.4[14]				
$ZnBr_{2(s)}$		-328.65[14]	159.7[14]				
4-cyanopy$_{(s)}$		40.9 ± 3.9[15]	83.6 ± 3.5[15]				
$[MnBr_2(4\text{-cyanopy})_2]_{(s)}$	-43.63 ± 1.42	-346.7 ± 8.2	83.6 ± 12[16]	-416.7 ± 7.4	210.8 ± 7.1	-333.1 ± 14.1	166.6 ± 7.1
$[FeBr_2(4\text{-cyanopy})]_{(s)}$	-25.07 ± 1.13	-234.0 ± 4.5	83.6 ± 12[16]	-313 ± 4	108.7 ± 3.7	-229 ± 13	229 ± 7
$[CoBr_2(4\text{-cyanopy})_2]_{(s)}$	-38.00 ± 1.08	-177.1 ± 4.5	83.6 ± 12[16]	-388 ± 7	205.2 ± 7.1	-305 ± 14	153 ± 7
$[NiBr_2(4\text{-cyanopy})_2]_{(s)}$	-53.00 ± 0.96	-183.3 ± 6.9	83.6 ± 12[16]	-390 ± 7	220.2 ± 7.1	307 ± 14	154 ± 7
$[CuBr_2(4\text{-cyanopy})_2]_{(s)}$	-39.48 ± 1.04	-99.5 ± 7.7	83.6 ± 12[16]	-389.1 ± 7.1	206.7 ± 7.1	-306 ± 14	153 ± 7
$[ZnBr_2(4\text{-cyanopy})_2]_{(s)}$	-53.40 ± 2.65	-300.3 ± 7.6	83.6 ± 12[16]	-380.3 ± 7.7	220.6 ± 7.5	-269.7 ± 14	148.4 ± 7.0

Table 6. Auxiliary Data and Enthalpy Changes of the Ionic Complex Formation Process in the Gaseous Phase ($kJ \cdot mol^{-1}$)

compound	$\Delta_f H^\theta$	$\Delta_r H^\theta(g)$	$\Delta_{fI} H^\theta$
$Br_{(g)}^{-}$	-219.07[18]		
$Mn_{(g)}^{2+}$	2522.0 ± 0.1[19]		
$Fe_{(g)}^{2+}$	2751.6 ± 2.3[19]		
$Co_{(g)}^{2+}$	2841.7 ± 3.4[19]		
$Ni_{(g)}^{2+}$	2930.5 ± 1.5[19]		
$Cu_{(g)}^{2+}$	3054.5 ± 2.1[19]		
$Zn_{(g)}^{2+}$	2781.0 ± 0.4[19]		
$[MnBr_2(4\text{-cyanopy})_2]_{(g)}$		-261 ± 18	-2594 ± 21
$[FeBr_2(4\text{-cyanopy})]_{(g)}$		-229 ± 13	-2589 ± 15
$[CoBr_2(4\text{-cyanopy})_2]_{(g)}$		-94 ± 18	-2747 ± 21
$[NiBr_2(4\text{-cyanopy})_2]_{(g)}$		-100 ± 18	-2841 ± 21
$[CuBr_2(4\text{-cyanopy})_2]_{(g)}$		-16 ± 18	-2881 ± 18
$[ZnBr_2(4\text{-cyanopy})_2]_{(g)}$		-217 ± 20	-2809 ± 23

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 $\bar{D}_{(M-N)} = (\Delta_r H^\theta(g)/n)$.[13] Table 5 lists the values obtained for these enthalpies. On the basis of the $\Delta_r H^\theta$ values for the adducts, the acidity order for the salts can be established: $ZnBr_2 \cong NiBr_2 > MnBr_2 > CuBr_2 \cong CoBr_2$. Using the $\bar{D}_{(M-N)}$ values, the order is $MnBr_2 > NiBr_2 \cong CoBr_2 \cong CuBr_2 > ZnBr_2$. Comparing the values of $\bar{D}_{(M-N)}$ with the values obtained for adducts of pyridine (py)[17] with the same stoichiometry, it can be observed that the basicity order of the ligands is py > 4-cyanopy, as would be expected due to the inductive effect of the substitution of one hydrogen atom in the pyridine ring by the electron-withdrawing cyano (CN) group. The enthalpies for the process of the adduct formation in the gaseous phase, from metal(II) ions, bromide ions, and 4-cyanopyridine molecules, can be evaluated:

$$M_{(g)}^{2+} + 2Br_{(g)}^{-} + n(4\text{-cyanopy})_{(s)} \rightarrow [MBr_2(4\text{-cyanopy})_n]_{(g)} \qquad \Delta_{fI} H^\theta \quad (6)$$

where

$$\Delta_{fI} H^\theta = \Delta_f H^\theta(\text{adduct}_{(g)}) - \Delta_f H^\theta(M_{(g)}^{2+}) - 2\Delta_f H^\theta(Br_{(g)}^{-}) - n\Delta_f H^\theta(4\text{-cyanopy}_{(g)})$$

Table 6 lists the values obtained for these enthalpy values. The correlation of these values with the metal atomic number is shown in Figure 1. Part of the double periodic variation profile is seen. The graphic allows us to determine the thermodynamic stabilization energy in the ligand field (LFSE) formed by two bromine ions and two nitrogen atoms from two ligand molecules, on the assumption that the course of variation of the enthalpy values is linear in a hypothetical state without the influence of the ligand field, being equal to the difference between the real and the interpolated values. Thus, the following is found: Co(II) (70 $kJ \cdot mol^{-1}$) < Ni(II) (120 $kJ \cdot mol^{-1}$) > Cu(II) (85 $kJ \cdot mol^{-1}$). Comparing with adducts with the same stoichiometry formed by Co(II) and Cu(II) bromides with β-picoline N-oxide (β-picoNO),[20] α-picoline N-oxide (α-picoNO),[21] and pyridine (py),[17] the following is observed: Co(II) at (72, 52, and 87) $kJ \cdot mol^{-1}$ and Cu(II) at (129, 174, and 174) $kJ \cdot mol^{-1}$. For the adduct of Ni(II) bromide with pyridine, a value of 124 $kJ \cdot mol^{-1}$ was obtained. Then, the LFSE follows the order α-picoNO < 4-cyanopy < β-picoNO < py for the Co(II) adducts, the order 4-cyanopy < β-picoNO < α-picoNO ≅ py for the

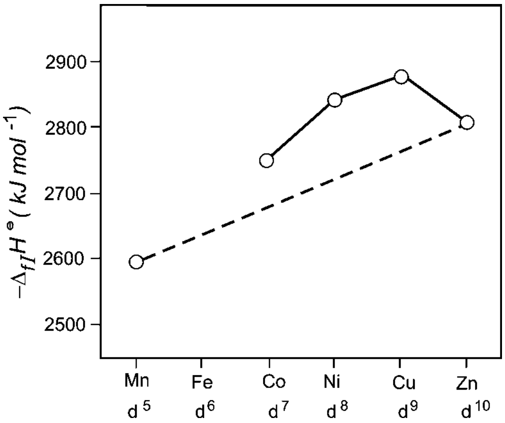

Figure 1. Plot of the enthalpy changes of complex formation in the gaseous phase from ionic components against a d-electron configuration.

Cu(II) adducts, and the order 4-cyanopy < py for the adducts of Ni(II). As a whole, the spectrochemical series of the ligands would be py > β-picoNO > 4-cyanopy > α-picoNO.

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