

Thermochemical parameters of 1,2,3,4-tetrahydroquinoline adducts of some divalent transition metal bromides

Pedro Oliver Dunstan*

Instituto de Química, Universidade Estadual de Campinas, Campinas, Brazil; *Corresponding Author: dunstan@iqm.unicamp.br

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ABSTRACT

The adducts $[MBr_2(L)_n]$, where $M = Fe, Co, Ni, Cu$ or Zn ; $L = 1,2,3,4$ -tetrahydroquinoline (THQ); $n = 0.75, 1$ or 2 have been obtained from the interaction in hot solution of THQ with the metal(II) bromides. The compounds were characterized by melting points, elemental analysis, thermal analysis and IR spectroscopy. From calorimetric studies in solution, the standard enthalpies of formation of them and several other thermochemical parameters were determined. The mean standard enthalpies of the metal(II)-nitrogen bonds have been estimated.

Keywords: Transition Metal Complexes; Thermochemistry; Coordinated Bonds Energies; Dissolution Enthalpies; Calorimetry

1. INTRODUCTION

Quinoline and quinoline derivatives are known to form complexes with transition metal(II) halides [1-23]. Thermochemical parameters related to the transition metal(II)-nitrogen coordinated bonds formed in these compounds are not found in the literature. In a recent article [23] it was determined the values for several thermochemical parameters of adducts of some transition metal(II) bromides with quinoline. Following with the purpose of filling the lack of information on the energy evolved in the formation of these compounds, in the present article, it is reported the calorimetric determination of the energy involved in the formation of the coordinated metal(II)-nitrogen bonds, as well as, the values of several thermochemical parameters for the compounds formed between some metal(II) bromides with tetrahydroquinoline. The knowledge of these energy values is very important for understanding the coordinated metal(II)-nitrogen bonds formed. The thermodynamic

properties of the compounds eventually could be used in determining their applications in catalysis and in the chromatographic separation of the metallic ions.

2. EXPERIMENTAL

1,2,3,4-Tetrahydroquinoline (98%, Aldrich) was purified by distillation through an efficient column and stored over Linde 4Å molecular sieves. All the anhydrous metal(II) bromides used in the preparation of the adducts were of reagent grade (99%+). Solvents used in the synthesis of the compounds and in calorimetric measurements were purified by distillation and stored over Linde 4Å molecular sieves.

2.1. Adducts Synthesis

The adducts were prepared by the interaction of metal (II) bromides and ligand in solution. It was used hot ethanol or hot methanol. It was used a molar ratio salt/ligand of 1/4 or 1/2. Following, the solvent was evaporated by using vacuum. The solid obtained was re-crystallized, washed with three portions of petroleum ether and dried in vacuum. A typical procedure is given below.

CoBr₂-THQ

To a solution of 1.0 g of CoBr₂ (4.57 mmol) in 50 mL of hot ethanol, 2.3 mL (18.29 mmol) of tetrahydroquinoline was added slowly and dropwise under stirring. After filtering and evaporation of the solvent, a green solid was obtained. This was re-crystallized from chloroform. The product was dried for several hours in vacuum and stored in a desiccator over calcium chloride.

2.2. Analytical and Physical Measurements

Carbon, hydrogen and nitrogen were determined by micro analytical procedures [24]. Halide analysis was made by gravimetry using standard N/10 AgNO₃ aqueous solution, after the adducts were dissolved in water

[25]. Metal contents were determined by complexometric titration with 0.01 M EDTA solution of aqueous solution of the adducts [26]. The capillary melting points of them were determined with a UNIMELT equipment from Thomas Hover. Spectra were obtained with samples in KBr matrix for the solid adducts. For tetrahydroquinoline, a film of the ligand sandwiched between KBr plates was used. A Perkin-Elmer 1600 series FT-IR spectrophotometer in the 4000 - 400 cm^{-1} region was used. TG/DTG and DSC measurements were obtained in argon atmosphere in a Du Pont 951 TG analyzer with the sample varying in mass from 5,58 to 19,94 mg (TG/DTG) and from 2,44 to 9,09 mg (DSC) and a heating rate of 10 $\text{K}\cdot\text{min}^{-1}$ in the 298 - 678 K (DSC) and 298-1248 (TG/DTG) temperature ranges. TG calibration for temperature was made with metallic aluminum as a standard ($\text{mp} = 660.37^\circ\text{C}$) and the equipment carried out the calibration for mass automatically. The DSC calibration was made with metallic indium as a standard ($\text{mp} = 165.73^\circ\text{C}$, $\Delta_s H^\theta = 28.4 \text{ J}\cdot\text{g}^{-1}$). 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. All the solution calorimetric measurements were carried out in an LKB 8700-1 calorimeter as described before [27]. The solution calorimetric measurements were performed by dissolving samples of 2.7 - 85.3 mg of the adducts or metal(II) bromides in 100 mL of 1.2 M

aqueous HCl and the ligand in this last solution maintaining a molar relation salt/ligand equal to the stoichiometry of the adduct. The accuracy of the calorimeter was checked by determining the heat of dissolution of tris [(hydroxymethyl)amino] methane in 0.1 $\text{mol}\cdot\text{dm}^{-3}$ HCl. The result ($-29.78 \pm 0.03 \text{ kJ}\cdot\text{mol}^{-1}$) is in agreement with the value recommended by IUPAC ($-29.763 \pm 0.003 \text{ kJ}\cdot\text{mol}^{-1}$) [28].

3. RESULTS AND DISCUSSION

3.1. Characterization of the Compounds

All the adducts were solids. The yields range from 22% to 60%. The capillary melting points and analytical data are summarized in **Table 1**.

3.1.1 Infrared Studies

The more important IR bands of the compounds are reported in **Table 2**. The spectra show shift of several bands after coordination with respect to the free ligand. Shifts to lower frequencies of the N-H stretching modes of the coordinated tetrahydroquinoline are observed. This is indicative of coordination to the metallic(II) ion through the nitrogen atom [13,29].

3.1.2. Thermal Studies

The thermogravimetry of the compounds shows the

Table 1. Melting points, yields, appearance and analytical data of the adducts.

Compound	Yield %	mp °C	% Calculated (found)				
			% C	% H	% N	% Br	% Metal
[FeBr ₂ (THQ) _{0.75}]	34	108-11	25.69(25.39)	2.64(2.71)	3.32(3.30)	50.65(50.75)	17.70(17.73)
[CoBr ₂ (THQ) ₂]	32	235-38	44.56(44.76)	4.57(4.47)	5.77(5.73)	32.94(32.90)	12.15(12.04)
[NiBr ₂ (THQ) _{1.5}]	89	368-71	38.76(38.98)	3.98(4.22)	5.02(4.97)	38.20(38.15)	14.03(13.99)
[CuBr ₂ (THQ) ₂]	5	95-98	44.15(43.85)	4.53(4.30)	5.72(5.62)	32.63(32.81)	12.97(13.01)
[ZnBr ₂ (THQ) ₂]	60	48-51	51.91(51.80)	5.32(5.23)	6.73(6.55)	25.58(25.69)	10.46(10.50)
[ZnBr ₂ (THQ) ₃]	22	pastry	43.98(43.70)	4.51(4.33)	5.70(5.57)	32.51(32.56)	13.30(13.34)

Table 2. Main IR spectral data (cm^{-1}) of the compounds.

Compound	Band assignments				
	$\nu_{\text{(N-H)}}$	$\nu_{\text{(C-C)}}$	$\delta_{\text{(N-H)}}$	Ring	$\phi_{\text{(C-C)}}$
THQ	3406s	1606s	1584m	1033m	747s
[FeBr ₂ (THQ) _{0.75}]	3386s, b	1558m	no	995m	753s
[CoBr ₂ (THQ) ₂]	3396m, b	1581m	1581m	957m	740s
[NiBr ₂ (THQ) _{1.5}]	3406m, 3054m	1557m	1606m	996m	752s
[CuBr ₂ (THQ) ₂]	3443s, 2923m	1594m	1594m	805m	779m
ZnBr ₂ (THQ) ₂]	3410s, 3224m	1535m	1588m	967m	749s
[ZnBr ₂ (THQ) ₃]	3408s, 3146m	1586m	1586m	1002m	750s

loss of part of the ligand in 2 - 4 steps of mass loss, alone or together with the loss of part of the bromine or with part of bromine and part of the metal content in the last step of mass loss. Bromine is lost in the last step or in the two final steps of mass loss, alone or together with the mass loss of part of the metal content. A residue is left that is part of the metal content. The DSC curves are consistent with the TG data. They present endothermic peaks due to the elimination of part of the ligand or part of bromine, alone or together with the elimination of part of the metal content. They present exothermic peaks due to the decomposition of the ligand or intermediate compounds. **Table 3** presents the thermoanalytical data of the adducts.

3.1.3 Electronic Spectra

The ligand field parameters for the cobalt adduct have been calculated according to Lever [30]. Considering the number and position of the bands [31,32] and according with the magnitude of the crystal field parameters as compared with that of Bolster [33], it is concluded that two nitrogen atoms from two ligand molecules and by two bromides ions pseudo-tetrahedrally surround Co(II) ion. The ligand field parameters for the Ni(II) adduct were calculated according to Reedijk *et al.* [34] and

Lever [30]. According to the number and position of the observed bands and considering the magnitude of the crystal field parameters as compared with that of Bolster [33], it is concluded that the Ni(II) ion is pseudo-tetrahedrally surrounded by two nitrogen atoms from two ligand molecules and two bromides ions, one of which is bridging to other Ni(II) ion in a dimeric structure. This last ion is surrounded by one nitrogen atom from one ligand molecule and three bromine ions, one of which is the mentioned bridge with the first nickel ion. For the Cu(II) adduct, the electronic spectra showed a rather broad asymmetrical band with maxima at 10528 cm^{-1} . Its intensity and position correspond with those observe for pseudo-octahedral compounds [33], with the Cu(II) ion being surrounded by two nitrogen atoms from two ligand molecules and by four bromide ions in a bridge structure. The ligand parameters for the adduct of Fe(II) were calculated according to Bolster [33]. It is concluded that one unit is formed by Fe(II) ion pseudo-octahedrally surrounded by one nitrogen atom from one ligand molecule and five bromide ions in a polymeric structure bridging with other units of Fe(II) ion surrounded by six bromide ions. **Table 4** contains the band maxima assignments and calculated ligand field parameters for the adducts.

Table 3. Thermal analysis of the compounds.

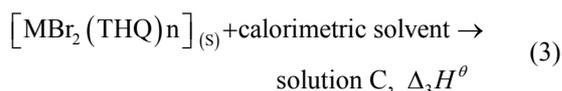
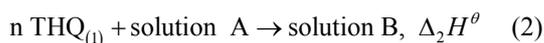
Compound	Apparent mp K	Mass loss (%)		TG temperature range K	Species lost	DSC peak temperature	ΔH^θ (kJ·mol ⁻¹)
		Calcd.	Obs.				
[FeBr ₂ (THQ) _{0.75}]	381-4	7.60	7.70	356 - 394	-0.18L	394	61.63
		24.05	24.82	394 - 562	-0.57L	507	1.59
		17.73	17.71	914 - 938	-0.70Br		
		25.33	25.73	938 - 1086	-Br		
[CoBr ₂ (THQ) ₂]	508-11		24.04	1248	residue		
		27.45	27.22	477 - 546	-L	342	2.73
		27.45	23.47	546 - 565	-L	516	27.44
		34.13	38.68	565 - 957	-2Br-0.1Co	530	6.48
[NiBr ₂ (THQ) _{1.5}]	368-71		10.63	1248	residue		
		16.72	16.39	369 - 409	-0.7L	387	71.16
		36.79	37.24	409 - 494	-1.3L-0.3Br	441	-75.95
		32.47	32.64	846-959	-1.7Br	490	90.66
[CuBr ₂ (THQ) ₂]	428-31		13.73	1248	residue		
		6.80	6.40	365 - 399	-0.25L	372	-19.40
		14.96	15.09	399 - 508	-0.55L	399	-1.22
		8.16	8.47	508 - 646	-0.30L	439	-28.63
[ZnBr ₂ (THQ) ₂]	321-4	61.00	60.80	646 - 1056	-0.90L-2Br-0.3Cu	499	1.59
			9.24	1248	residue		
		35.22	35.48	228-544	-1.3L	357	31.15
		54.13	54.31	544-742	-0.7L-2Br-0.2Zn	284	-5.08
[ZnBr ₂ (THQ) ₃]	pastry	8.65	8.28	742-1069	-0.65Zn	496	-3.24
			1.93	1248	residue		
		42.64	44.20	392 - 526	-2L	320	27.22
		34.11	36.16	526 - 732	-L-Br	448	-28.86
[ZnBr ₂ (THQ) ₃]	pastry	12.79	10.25	813 - 831	-Br		
		6.28	5.11	831 - /1020	-0.60Zn		
			4.28	1248	residue		

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

Compound	Band maxima ($\times 10^3 \text{ cm}^{-1}$)						Intraligand + charge transfer	
	d-d							
[FeBr ₂ (THQ) _{0.75}]	10.60						21.17	
	ν_2	ν_3	Dq (cm ⁻¹)	B(cm ⁻¹)	Dq/B	$\beta(B/B_0)[33]$		
[CoBr ₂ (THQ) ₂]	7.36	15.28	431	648	0.665	0.667	20.63	32.65
[NiBr ₂ (THQ) _{1.5}]	8.38	14.28	243	1272	0.191	1.235	21.77	
[CuBr ₂ (THQ) ₂]	10.53						23.78	34.83

3.1.4. Calorimetric Measurements

The standard enthalpies of dissolution of metal(II) bromides, tetrahydroquinoline and adducts were obtained as previously reported [27]. The standard enthalpies of dissolution were obtained according to the standard enthalpies of the following reactions in solution:



The application of 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:



where $\Delta_r H^\theta = \Delta_1 H^\theta + \Delta_2 H^\theta - \Delta_3 H^\theta$ 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 MBr₂ ($\Delta_1 H^\theta$), THQ into the solution of MBr₂ ($\Delta_2 H^\theta$) and of the adducts ($\Delta_3 H^\theta$). Uncertainty intervals given in this table are twice the standard deviation of the mean of 4 - 9 replicate measurements. The thermochemical parameters 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 [29], 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 later values can be used to calculate the standard enthalpies of the M-N bonds, being equal to $\bar{D}_{(M-N)} = -\Delta_r H^\theta(g)/n$ [35]. **Table 6** lists the values of all these thermochemical parameters. The standard enthalpies of: formation and

Table 5. Enthalpies of dissolution at 298.15 K.

Compound	Calorimetric solvent	Number of experiments	i	$\Delta_r H^\theta$ (kJ·mol ⁻¹)
FeBr _{2(s)}	1.2 M aq. HCl	5	1	-76.82 ± 1.12
THQ _(l)	0.75:1 FeBr ₂ -1.2 M aq. HCl	6	2	-21.45 ± 0.60
[FeBr ₂ (THQ) _{0.75}] _(s)	1.2 M aq. HCl	5	3	-13.04 ± 0.42
CoBr _{2(s)}	1.2 M aq. HCl	5	1	-57.92 ± 0.43
THQ _(l)	2:1 CoBr ₂ -1.2 M aq. HCl	6	2	-58.12 ± 1.75
[CoBr ₂ (THQ) ₂] _(s)	1.2 M aq. HCl	4	3	-32.72 ± 0.28
NiBr _{2(s)}	1.2 M aq. HCl	4	1	-64.79 ± 1.48
THQ _(l)	1.5:1 NiBr ₂ -1.2 M aq. HCl	5	2	-46.64 ± 2.13
[NiBr ₂ (THQ) _{1.5}] _(s)	1.2 M aq. HCl	5	3	6.32 ± 0.40
CuBr _{2(s)}	1.2 M aq. HCl	8	1	-24.40 ± 1.02
THQ _(l)	2:1 CuBr ₂ -1.2 M aq. HCl	5	2	-52.68 ± 0.42
[CuBr ₂ (THQ) ₂] _(s)	1.2 M aq. HCl	4	3	-11.56 ± 0.73
ZnBr _{2(s)}	Ethanol	9	1	-43.59 ± 0.50
THQ _(l)	2:1 ZnBr ₂ -Ethanol	5	2	5.46 ± 0.16
[ZnBr ₂ (THQ) ₂] _(s)	Ethanol	4	3	25.46 ± 1.08
THQ _(l)	3:1 ZnBr ₂ -Ethanol	5	2	8.30 ± 0.17
[ZnBr ₂ (THQ) ₃] _(s)	Ethanol	3	3	35.80 ± 1.60

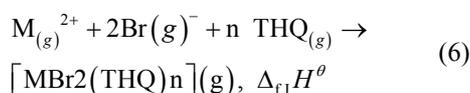
Table 6. Summary of the thermochemical results (KJ·mol⁻¹) for the compounds.

Compound	$\Delta_f H^\theta$	$\Delta_f H^\theta$	$\Delta_{s,i}^\theta H^\theta$	$\Delta_M H^\theta$			
FeBr _{2(s)}		-249.8 [36]	204 [37]				
CoBr _{2(s)}		-220.9 [36]	183 [37]				
NiBr _{2(s)}		-212.1 [36]	170 [37]				
CuBr _{2(s)}		-141.8 [36]	182.4 [37]				
ZnBr _{2(s)}		-328.65 [36]	159.7 [37]				
THQ _(l)		38.15	59.22				
[FeBr ₂ (THQ) _{0.75}] _(s)	-85.27 ± 1.34	-306.5 ± 2.5	132 ± 16 [38]	-318 ± 2	113.88 ± 2.41	-186 ± 16	248 ± 21
[CoBr ₂ (THQ) ₂] _(s)	-83.32 ± 1.82	-227.9 ± 2.9	121 ± 15 [38]	-385 ± 3	201.76 ± 2.70	-264 ± 15	132 ± 8
[NiBr ₂ (THQ) _{1.5}] _(s)	-105.11 ± 2.62	-260.0 ± 3.2	115 ± 14 [38]	-331 ± 3	162.34 ± 3.02	-217 ± 14	145 ± 9
[CuBr ₂ (THQ) ₂] _(s)	-65.52 ± 1.32	-131.0 ± 3.1	120.8 ± 14.5 [38]	-324.2 ± 2.6	-141.82 ± 2.40	-203.4 ± 14.7	101.7 ± 7.4
[ZnBr ₂ (THQ) ₂] _(s)	-63.59 ± 1.20	-315.94 ± 3.07	109.5 ± 13.1 [38]	-341.7 ± 3.1	182.03 ± 2.33	-232.2 ± 13.5	116.1 ± 6.8
[ZnBr ₂ (THQ) ₃] _(s)	-71.09 ± 1.68	-285.29 ± 3.98	109.5 ± 13.1 [38]	-408.5 ± 4.0	248.75 ± 3.43	-299.0 ± 13.7	99.7 ± 4.6

Table 7. Auxiliary data and enthalpy changes of the ionic complex formation process in the gaseous phase (KJ·mol⁻¹).

Compound	$\Delta_f H^\theta$	$\Delta_n H^\theta$	
Br ⁻ _(g)	-219.07 [36]		
Fe ²⁺ _(g)	2751.6 ± 2.3 [39]		
Co ²⁺ _(g)	2841.7 ± 3.4 [39]		
Ni ²⁺ _(g)	2930.5 ± 1.5 [39]		
Cu ²⁺ _(g)	3054.5 ± 2.1 [39]		
Zn ²⁺ _(g)	2781.0 ± 0.4 [39]		
[FeBr ₂ (THQ) _{0.75}] _(g)	-362 ± 16	-186 ± 16	-2748 ± 16
[CoBr ₂ (THQ) ₂] _(g)	-107 ± 15	-264 ± 15	-2705 ± 16
[NiBr ₂ (THQ) _{1.5}] _(g)	-113 ± 14	-217 ± 14	-2751 ± 14
[CuBr ₂ (THQ) ₂] _(g)	31.9 ± 15.0	203.4 ± 14.7	-2778.9 ± 15.4
[ZnBr ₂ (THQ) ₂] _(g)	-206.5 ± 13.7	-232.2 ± 13.5	-2741.1 ± 13.9
[ZnBr ₂ (THQ) ₃] _(g)	-175.9 ± 14.1	-299.0 ± 13.7	-2810.9 ± 14.6

sublimation of THQ as these values are not found in the literature. They were calculated by a group contribution method, from the enthalpies values for quinoline [40-42]. The enthalpies for the process of hypothetical monomer complex formation in the gaseous phase, from metal(II) ions, bromide ions and THQ molecules can be evaluated:



where $\Delta_f H^\theta = \Delta_f H^\theta(\text{adduct}_{(g)}) - \Delta_f H^\theta(M_{(g)}^{2+}) - 2\Delta_f H^\theta(Br_{(g)}^{-}) - n\Delta_f H^\theta(THQ_{(g)})$.

Table 7 lists the values obtained for these enthalpies values.

4. CONCLUSIONS

The interaction of transition metal(II) bromides with tetrahydroquinoline produced solid adducts of defined stoichiometry. The calorimetric study of them determined the standard enthalpies of formation and several other thermochemical parameters. The mean standard enthalpies of metal(II)-nitrogen coordinate bonds have values from 100 to 248 KJ·mol⁻¹. Comparing with the values obtained for quinoline adducts of metal(II) bromides of the same stoichiometry [23], it is observed that the bonds formed by THQ are weaker than the bonds

formed by quinoline. This means that the hydrogenation of the heterocycle of quinoline to get THQ leads to the weakness of the bond formed by the nitrogen atom with metal(II) ions. The basicity order of the ligands is: THQ < quinoline. Based on the $\Delta_r H^\theta$ values obtained for the adducts, the acidity order of the salts, for the adducts of the same stoichiometry can be established: $\text{CoBr}_2 > \text{CuBr}_2 > \text{ZnBr}_2$. Using the $\bar{D}_{(M-N)}$ values, the order is: $\text{CoBr}_2 > \text{ZnBr}_2 > \text{CuBr}_2$.

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