

Thermochemical Parameters of Tetramethylthiourea Adducts of Certain Metal(II) Bromides

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Abstract

Complexes of the general formula $[MBr_2(TMTU)_n]$ (where M is Mn, Fe, Co, Ni, Cu, Zn or Cd; TMTU is Tetramethylthiourea; n is 0.75, 2 or 3) were obtained by the reaction of salts and ligand in solution. The bromides were selected among several other salts because they had thermochemical data in the literature. Properties as capillary melting points; C, H, N, Br and metal contents; TG/DTG and DSC curves; and IR and electronic spectra were determined. The values of several thermodynamic parameters for the complexes were found by solution calorimetry. From them, the standard enthalpies of the metal-sulphur coordinated bonds were calculated. The standard enthalpies of the formation of the gaseous phase adducts also were estimated.

Keywords

Enthalpies of Formation, Thermodynamic, Coordinated Bond Enthalpies, Solution Calorimetry, Dissolution Enthalpies, Tetramethylthiourea Adducts

1. Introduction

Complexes formed by salts of transition and representative elements with thioamides are mentioned in the literature. M. V. Raja *et al.* [1] studied thioamide complexes of aryl bromides. R. Sah *et al.* [2] synthesized and characterized transition Metal(II) complexes of heterocyclic thiomides. H. Ajaz *et al.* [3] got the crystal structure of complexes of Antimony(II) with thioamides. T. Singh *et al.* [4] studied thioamide complexes of ruthenium. S. Nadeem *et al.* [5] studied thioamide complexes of Palladium(II) bromides. I. I. Ozturki *et al.* [6] characterized thioamide complexes of Antimony(III) bromide. J. Sola *et al.* [7] studied thioamide complexes of Silver(I) ion. L. S. Sbirna *et al.* [8] studied several complexes of transition metals with bidentated heterocyclic (N, S) ligands.

S. K. Misra *et al.* [9] studied the complexing behavior of thioamide in several transition metal complexes. V. Muresan [10] prepared new thioamide complexes of transition metals. C. Neagoe [11] *et al.* studied tertiary thioamide complexes of transition metals. F. Zalaru *et al.* [12] synthesized thioamide complexes of Cu(II). P. O. Dunstan *et al.* [13] characterized thioamide complexes of arsenic trihalides. H. O. Desseyn [14] studied chelates of thioamides. S. Neagoe *et al.* [15] studied thioamide complexes of transition metals. C. E. Carraher Jr. *et al.* [16] studied complexes of polythioamides with Palladium(II). B. Singh [17] studied thioamide complexes of Oxovanadium(IV). G. R. Burns *et al.* [18] studied thioamide complexes of Chromium(III). J. M. Bret *et al.* [19] studied thioamide complexes of platinum. V. Muresan *et al.* [20] prepared several thioamide complexes of transition metals. Yu. N. Kukushkin *et al.* [21] studied thioamide complexes of Platinum(I). A. J. Aarts *et al.* [22] studied thioamide complexes of Palladium(II). V. V. Sibirskaya *et al.* [23] prepared thioamide complexes of platinum metals. M. Molina *et al.* [24] studied the interaction of thioamides with metals. J. G. H. Du Preez *et al.* [25] studied thioamide complexes of oxovanadium dichloride.

In this work, complexes formed by tetramethylthiourea with bromides of Manganese(II), Iron(II), Cobalt(II), Nickel(II), Copper(II), Zinc(II) and Cadmium(II) were studied. Thermodynamic data found in the literature concerning the standard enthalpies of formation of coordinated bonds in this kind of complexes are limited. The knowledge of the thermodynamic properties of these compounds is important to find their applications in catalysis and in the chromatographic separation of metal ions. It could be inferred the affinity order of the metallic ions for stationary-movable chromatographic phases by the knowledge of the formation enthalpies of complexes. Also, the thermochemical parameters can be used in catalysis for finding the more adequate complex to accelerate a given reaction. In this article, calorimetric measurements were made to measure the strength of the metal-sulphur coordinated bonds. Correlations of the thermodynamic properties of the complexes were got. The enthalpies of formation of the complexes derived from the gaseous-phase metal ions, bromide ions and tetramethylthiourea were determined.

2. Materials and Methods

2.1. Reagents

Tetramethylthiourea (RP, Fluka AG Buchs SG) was purified by recrystallization from methanol (MP 75°C - 76°C). The anhydrous Metal(II) bromides used in the synthesis of the complexes were of analytical grade. Solvents were distilled and stocking over Linde 4Å molecular sieves before using.

2.2. Experimental Procedure

The complexes were prepared by the reaction between Metal(II) bromides and tetramethylthiourea in a molar ratio salt/ligand of 1/4 in hot tert-butyl alcohol solution or in a hot mixture ethanol/chloroform solution. Following, an example of one preparation: 1.00 g of NiBr₂ (4.58 mmol) was dissolved in 25 mL of hot tert-butyl alcohol and 2.41 g (18 mmol) of tetramethylthiourea was dissolved in 20 mL of hot tert-butyl alcohol. The later solution was poured into the solution of the salt, slowly and dropwise with stirring. The mixture was refluxed by five hours after which, the solid that formed was filtered and washed with 60 mL of petroleum ether divided in three portions. The compound obtained was maintained in a vacuum over twelve hours. It was stocked in desiccator over CaCl₂. The chemical analysis confirmed the contains proposed by the assumed stoichiometries. Microanalytical procedures [26] were used for the determination of C, H and N contents. Gravimetric analysis [27] was used to determine the bromine contents. The metal contents were complexometrically determined by using 0.01 M ethylenediaminetetraacetic acid solution [28]. Samples of the compounds in a KBr matrix were used to get the IR spectra. The region of spectra was from 4000 to 400 cm⁻¹ and a Perkin Elmer 1600 series FTIR spectrophotometer was used. A UV-Vis-NIR spectrophotometer was used to record the spectra of the solid compounds in the region 350 - 2000 nm using a standard reflectance attachment to get the spectra. TG/DTG and DSC curves were recorded in an argon atmosphere in a Du Pont 951 analyzer. The mass of the compounds was initially between 6.37 and 8.79 mg (TG/DTG) and from 4.80 to 16.14 mg (DSC). A heating rate of 10 K·min⁻¹ was used from 298 to 678 K (DSC) and from 298 to 1248 K (TG/DTG). The calibration for temperatures was conducted with metallic aluminum as a standard (MP = 933.49 K). The equipment performed the calibration for mass automatically. The DSC calibration was made with metallic indium as a standard (MP = 438.85 K, $\Delta_s H^\circ = 28.4 \text{ J}\cdot\text{g}^{-1}$). For the calorimetric study of the complexes, an LKB 8700-1 precision calorimeter was used at the

measurements temperature of 298.15 ± 0.02 K. A thin-walled ampoule that contained reactant was broken in a glass reaction vessel filled with (100.00 mL) of calorimetric solvent [29]. The accuracy of the equipment was determined as previously reported [29] [30]. Three to eight replicate measurements were made on each compound and the uncertainty intervals are twice the standard deviations. The experimental deviations of the dissolution measurements stated between (1% - 3%).

3. Results

3.1. Complex Characterization

The interaction of MBr_2 with TMTU in solution leads to compounds of definite stoichiometry. Only in the case of $FeBr_2$ the compound formed had a fractional stoichiometry. The yields (Y), capillary melting points (MP), colors, appearance (A) and analytical data are reported in **Table 1**.

3.2. Infrared Studies

Table 2 presents the main IR bands of the complexes. A strong band is observed in the region $1097 - 1148$ cm^{-1} . This band is attributed to the C=S stretching frequency (ν_{CS}) [31]. It is observed in the complexes relative to the free ligand, negative shifts of this frequency and positive shifts of the ν_{CN} frequency after coordination, indicating coordination of the ligand through the sulphur atom to the Metal(II) bromide [31]. **Figure 1** presents the IR spectra of the Zn(II) complex.

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

Compound ^a	Y %	MP ^a °C	A ^b	%C		%H		%N		%Br		%M	
				Cal.	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.
[MnBr ₂ (L) ₂]	76	150 - 52	y. p.	25.06	25.04	5.05	4.64	11.69	11.54	33.35	33.00	11.46	11.66
[FeBr ₂ (L) _{0.75}]	49	165 - 68	b. re. pa.	14.31	14.17	2.88	3.03	6.67	6.53	50.76	50.55	17.74	17.66
[CoBr ₂ (L) ₃]	86	82 - 84	gr. p.	29.27	29.57	5.90	5.95	13.66	13.98	25.97	25.38	9.58	9.88
[NiBr ₂ (L) ₂]	62	160 - 62	g. p.	24.87	24.54	5.01	4.96	11.60	11.21	33.09	33.45	12.16	12.04
[CuBr ₂ (L) ₂]	43	80 - 82	g. p.	24.62	24.87	4.96	5.35	11.49	11.85	32.76	33.01	13.03	13.25
[ZnBr ₂ (L) ₂]	74	158 - 60	w. p.	24.53	24.75	4.94	5.04	11.44	11.45	32.64	32.40	11.35	11.62
[CdBr ₂ (L) ₂]	86	169 - 71	w. p.	22.38	22.52	4.51	4.74	10.44	10.37	29.78	29.51	20.94	21.07

^aMelting with decomposition. ^bKey: y., yellow; b., brown; g., green; w., white; re., redish; gr., greenish; p., powder; pa., paste; ^{*}L = TMTU.

Table 2. IR absorption bands (cm^{-1}) of the compounds.

Compound	Assignment ^a $\nu_{(CS)}$	$\nu_{(CN)}$
TMTU	1120s	1511s, 1372s
[MnBr ₂ (TMTU) ₂]	1098s	1513m, 1367s
[FeBr ₂ (TMTU) _{0.75}]	1067s	1532w, 1393m
[CoBr ₂ (TMTU) ₃]	1109s	1558s, 1377s
[NiBr ₂ (TMTU) ₂]	1098s	1512m, 1361s
[CuBr ₂ (TMTU) ₂]	1114s	1537s, 1380s
[ZnBr ₂ (TMTU) ₂]	1110s	1557s, 1382s
[CdBr ₂ (TMTU) ₂]	1108s	1556s, 1390s

^a ν , stretching. Intensity of bands: s, strong; m, medium; w, weak.

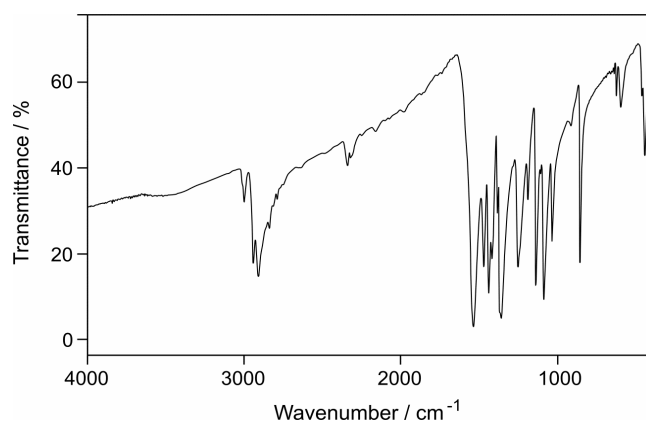


Figure 1. Infrared spectrum of the complex $[\text{ZnBr}_2(\text{TMTU})_2]$.

3.3. Thermal Studies

The thermogravimetry of the complex of Mn(II) shows the loss of the ligand in three steps of mass loss. In a fourth step it loses part of the bromine content leaving a residue that is part of the bromine content plus the metal content. The complex of Fe(II) shows the loss of the ligand in three steps. Part of the bromine content is lost together with part of the ligand in the third step of mass loss. Part of the bromine content is lost in the fourth and fifth steps of mass loss leaving a residue that is part of the bromine content plus the metal content. The complex of Co(II) shows the loss of ligand in three steps of mass loss. Part of the bromine content is lost together with part of the ligand in the third step. Part of the bromine content is lost in a fourth step of mass loss leaving a residue that is part of the bromine content plus the metal content. The complex of Ni(II) shows the loss of the ligand in the first step of mass loss follow by the loss of part of the bromine content in a second step of mass loss leaving a residue that is part of the bromine content plus the metal content. The complex of Cu(II) shows the loss of the ligand in the first step of mass loss together with part of the bromine content. The rest of the bromine content together with part of the metal content is lost in the second step of mass loss leaving a residue that is part of the metal content. The complex of Zn(II) shows the loss of the ligand in three steps of mass loss. The bromine content is lost together with part of the metal in the third step of mass loss. Part of the metal content is lost in the fourth step of mass loss leaving a residue that is part of the metal content. The complex of Cd(II) shows the loss of the ligand in two steps of mass loss follow by the loss of the bromine content and part of the metal content in the third step of mass loss leaving a residue that is part of the metal content. **Figure 2** presents the TG/DTG curve of the Co(II) complex. The DSC curves of the complexes are consistent with the TG data. They present endothermic peaks due to the elimination of part of the ligand or part of the bromine content alone or together with part of the ligand. An exothermic peak is observed in the DSC curve of the Fe(II) complex due to the decomposition of the complex. **Figure 3** presents the DSC curve of the Co(II) complex. **Table 3** presents the thermoanalytical data for the complexes.

3.4. Electronic Spectra

The ligand field parameters for the Ni(II) complex were calculated according to Reedijk *et al.* [32] and Lever [33]. The number and position of the observed bands and the magnitude of the crystal field parameters as compared with that of Bolster [34] indicates that the Ni(II) complex is pseudo-tetrahedral with the Ni(II) ion surrounded by two bromide ions and two sulphur atoms from two ligand molecules. The Co(II) complex shows bands attributed to pseudo-octahedral species with Co(II) ion surrounded by three bromide ions and three sulphur atoms from three ligand molecules in a dimeric structure of bridging bromide ions. The ligand field parameters were calculated according to Lever [33]. The electronic spectra of Cu(II) complex shows a rather broad and symmetrical band which position according to Bolster [34] corresponds to pseudo-tetrahedral species with the Cu(II) ion surrounded by two bromide ions and two sulphur atoms from two ligand molecules. The ligand field parameters of the Fe(II) complex were calculated according to Bolster [34]. It is concluded that Fe(II) ion is pseudo-octahedral with units $[\text{FeBr}_6]^{4-}$ and $[\text{FeBr}_5\text{L}]^{3-}$ in a molar relation of 1:3 in a polymeric chain of

Table 3. Thermal analysis of the compounds.

Compound ^a	Apparent MP/K	Mass loss/%		TG temperature range/K	Species lost	DSC peak temperature	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$
		Calcd.	Obs.				
[MnBr ₂ (L ₂)	423 - 25	1.93	1.84	325 - 353	-0.07L	346	1.53
		38.65	38.21	353 - 487	-1.41L	421	35.99
		14.63	16.19	487 - 564	-0.53L		
		28.34	28.39	884 - 962	-1.7Br		
			15.00 ^a				
[FeBr ₂ (L) _{0.75}]	438 - 41	9.00	8.67	375 - 494	-0.21L	349	-5.66
		13.50	12.72	494 - 531	-0.32L	413	2.33
		26.26	26.08	531 - 700	-0.22L - 0.68Br	469	1.33
		19.29	19.69	700 - 858	-0.76Br	510	0.32
		4.06	4.07	858 - 915	-0.16Br		
	28.77 ^a						
[CoBr ₂ (L ₃)	355 - 57	25.79	25.53	353 - 389	-1.20L	340	30.36
		26.86	26.61	389 - 538	-1.25L	385	9.77
		15.71	16.03	538 - 564	-0.55L - 0.3Br		
		18.17	18.67	564 - 861	-1.4Br		
	13.16 ^a						
[NiBr ₂ (L ₂)	433 - 35	54.76	55.24	428 - 505	-2L	393	1.09
		28.12	27.44	505 - 890	-1.7Br	427	27.48
			17.32 ^a			442	21.49
[CuBr ₂ (L) ₂]	353 - 55	70.60	68.07	398 - 484	-2L - Br	352	38.19
		26.80	26.76	484 - 838	-Br - 0.8Cu	441	2.62
			5.17 ^a				
[ZnBr ₂ (L) ₂]	433 - 35	35.10	35.09	434 - 591	-1.3L	430	38.51
		13.54	13.24	591 - 615	-0.5L		
		46.05	46.26	615 - 760	-0.2L - 2Br - 0.6Zn		
		1.34	0.83	760 - 942	-0.1Zn		
	4.58 ^a						
[CdBr ₂ (L) ₂]	442 - 44	36.96	36.62	412 - 570	-1.5L	434	42.08
		12.32	13.15	570 - 580	-0.5L		
		49.67	49.12	784 - 838	-2Br - 0.95Cd		
			1.11 ^a				

^aResidue at 1243 K; ^bL = TMTU.

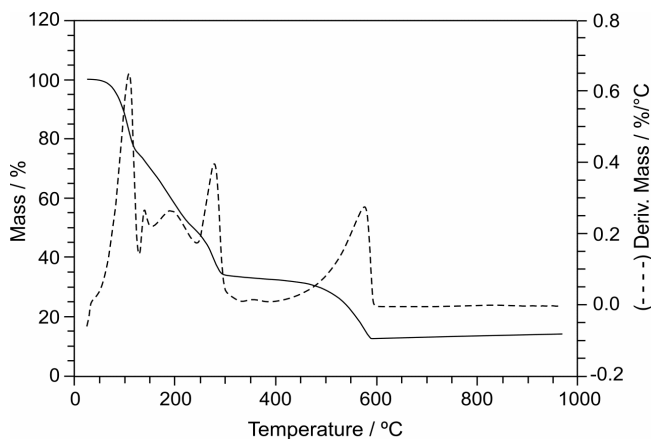


Figure 2. TG/DTG curve of the complex $[\text{CoBr}_2(\text{TMTU})_3]$.

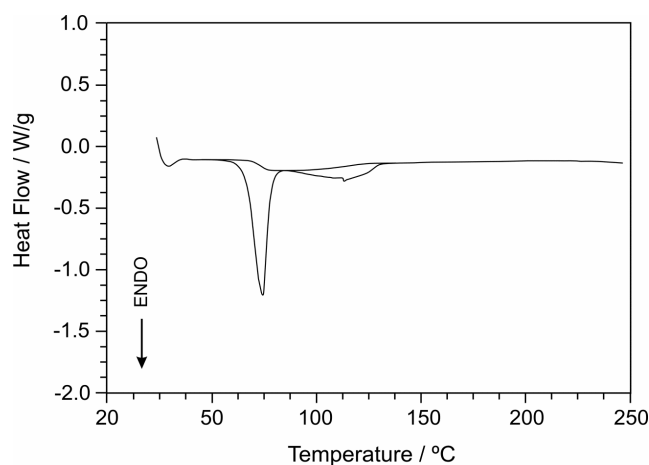
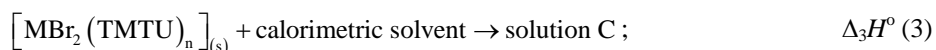
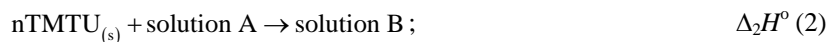
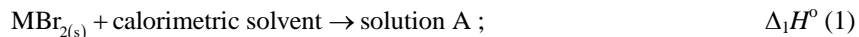


Figure 3. DSC curve of the complex $[\text{CoBr}_2(\text{TMTU})_3]$.

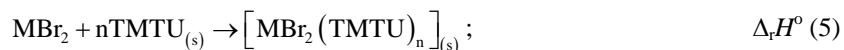
bridging bromide ions. The complex of Mn(II) according with the position of the absorption band [34] is pseudo-tetrahedral with the manganese ion surrounded by two bromide ions and two sulphur atoms from two ligand molecules. **Table 4** contains the band maxima assignments and calculated ligand field parameters of the complexes.

3.5. Calorimetric Measurements

The standard enthalpies of dissolution of Metal(II) bromides, TMTU and complexes were measured [35]. The standard enthalpies of the following reactions were obtained:



The application of the Hess' law to the reactions 1 to 4 gives the standard enthalpies of reaction ($\Delta_r H^\circ$):



being $\Delta_r H^\circ = \Delta_1 H^\circ + \Delta_2 H^\circ - \Delta_3 H^\circ$, because $\Delta_4 H^\circ = 0$ for the dissolution of solution B into solution C. **Table 5**

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

Complex ^a	Band maxima ($\times 10^3 \text{ cm}^{-1}$)		Interligand + charge transfer ($\times 10^3 \text{ cm}^{-1}$)					
	d-d							
[MnBr ₂ (L) ₂]	21.37, 26.32							31.95
[CuBr ₂ (L) ₂]	12.50							26.81
	ν_1	Dq (cm^{-1})						
[FeBr ₂ (L) _{0.75}]	7.26 ^a	726						
	ν_1	ν_2	ν_3	Dq (cm^{-1})	B	Dq/B	β^+	
[CoBr ₂ (L) ₃]	7.66 ^b	13.46 ^c	19.08 ^d	580	1002	0.579	1.032	19.08, 20.75, 26.95
[NiBr ₂ (L) ₂]	9.07 ^e	15.20 ^f	236	275	0.858	0.267		21.93

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

Table 5. Enthalpies of dissolution at 298.15 K.

Compound	Calorimetric solvent	Number of experiments	i	$\Delta_r H^\circ$ ($\text{kJ} \cdot \text{mol}^{-1}$)
MnBr _{2(s)}	1.2 M HCl	5	1	-43.96 ± 1.73
TMTU _(s)	2:1 MnBr ₂ - 1.2 M HCl	4	2	21.99 ± 1.41
[MnBr ₂ (TMTU) ₂] _(s)	1.2 M HCl	3	3	-20.06 ± 0.74
CoBr _{2(s)}	1.2 M HCl	6	1	-69.83 ± 0.80
TMTU _(s)	3:1 CoBr ₂ - 1.2 M HCl	4	2	30.10 ± 1.80
[CoBr ₂ (TMTU) ₃] _(s)	1.2 M HCl	4	3	21.97 ± 0.62
NiBr _{2(s)}	1.2 M HCl	5	1	-55.59 ± 2.11
TMTU _(s)	2:1 NiBr ₂ - 1.2 M HCl	4	2	24.05 ± 1.73
[NiBr ₂ (TMTU) ₂] _(s)	1.2 M HCl	4	3	-19.86 ± 0.88
CuBr _{2(s)}	1.2 M HCl	6	1	-24.63 ± 1.54
TMTU _(s)	2:1 CuBr ₂ - 1.2 M HCl	3	2	14.11 ± 0.63
[CuBr ₂ (TMTU) ₂] _(s)	1.2 M HCl	4	3	30.38 ± 0.80
ZnBr _{2(s)}	1.2 M HCl	8	1	-42.23 ± 0.88
TMTU _(s)	2:1 ZnBr ₂ - 1.2 M HCl	4	2	19.80 ± 0.81
[ZnBr ₂ (TMTU) ₂] _(s)	1.2 M HCl	3	3	19.40 ± 0.46
CdBr _{2(s)}	1.2 M HCl	5	1	23.83 ± 2.79
TMTU _(s)	2:1 CdBr ₂ - 1.2 M HCl	4	2	19.95 ± 0.23
[CdBr ₂ (TMTU) ₂] _(s)	1.2 M HCl	3	3	62.78 ± 1.32

presents the values observed for the enthalpies of dissolution of MBr₂($\Delta_1 H^\circ$), for the enthalpies of dissolution of TMTU into the solution of MBr₂($\Delta_2 H^\circ$) and that of the complexes ($\Delta_3 H^\circ$). It was not possible to measure the enthalpies of dissolution of the complex of Fe(II) due to its paste consistency that made it difficult its manipulation. Uncertainty intervals given in this table are twice the standard deviations of the mean of 3 to 8 replicate measurements.

4. Discussions

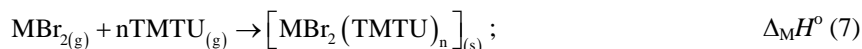
Using the standard enthalpies of reaction ($\Delta_r H^\circ$) and appropriate thermochemical cycles [35], the following thermochemical parameters were got: the standard enthalpies of formation ($\Delta_f H^\circ$) from Equation (5),

$$\Delta_f H^\circ (\text{complex}) = \Delta_r H^\circ + \Delta_r H^\circ (\text{MBr}_{2(s)}) + n\Delta_f H^\circ (\text{TMTU}_{(s)})$$

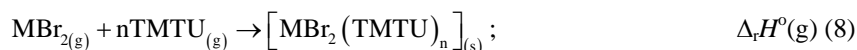
the standard enthalpies of decomposition ($\Delta_D H^\circ$) from Equation (6),



being $\Delta_D H^\circ = \Delta_r H^\circ + n\Delta_s^\circ H^\circ (\text{TMTU}_{(s)})$. The standard lattice enthalpy ($\Delta_M H^\circ$), from Equation (7),



being $\Delta_M H^\circ = -\Delta_D H^\circ - \Delta_s^\circ H^\circ (\text{MBr}_{2(s)})$. The enthalpy of reaction in the gaseous phase, from Equation (8)



being $\Delta_r H^\circ (g) = -\Delta_s^\circ H^\circ (\text{MBr}_{2(s)}) - n\Delta_s^\circ H^\circ (\text{TMTU}_{(s)}) + \Delta_r H^\circ + \Delta_s^\circ H^\circ (\text{complex}_{(s)})$.

As the complexes decomposed on heating, the enthalpies of sublimation of the complexes were estimated [36].

From Equation (8) it is got the standard enthalpies of the metal-sulphur bonds: $D_{(M-S)} = -(\Delta_r H^\circ (g))/n$. **Table 6** presents the values obtained for all these enthalpies. The formation enthalpies of the complexes in the gaseous phase, according to the Equation (9)



are equal to $\Delta_f H^\circ = \Delta_r H^\circ (\text{complex}) - \Delta_f H^\circ (\text{M}_{(g)}^{2+}) - 2\Delta_f H^\circ (\text{Br}_{(g)}^-) - n\Delta_f H^\circ (\text{TMTU}_{(g)})$. **Table 7** shows the values obtained for these enthalpies values.

The acidity order obtained based on $\Delta_r H^\circ$ values for the complexes of the same stoichiometry is: Zn(II) > Cu(II) > Cd(II) > Ni(II) > Mn(II). Using the $D_{(M-S)}$ values the, order is: Cu(II) > Zn(II) > Mn(II) > Ni(II) > Cd(II).

Table 6. Summary of the thermochemical results ($\text{kJ}\cdot\text{mol}^{-1}$) for the compounds.

Compound	$\Delta_r H^\circ$	$\Delta_f H^\circ$	$\Delta_s^\circ H^\circ$	$\Delta_M H^\circ$	$\Delta_D H^\circ$	$\Delta_r H^\circ(g)$	$D_{(M-S)}$
MnBr _{2(s)}		-384.9 ^a	205.9 ^a				
CoBr _{2(s)}		-220.9 ^a	183 ^a				
NiBr _{2(s)}		-212.1 ^a	170 ^a				
CuBr _{2(s)}		-141.8 ^a	182.4 ^a				
ZnBr _{2(s)}		-328.65 ^a	159.7 ^a				
CdBr _{2(s)}		-316.2 ^b	151.2 ^c				
TMTU _(s)		-38.3 ± 2.3 ^d	82.36 ± 0.20 ^d				
[MnBr ₂ (TMTU) ₂] _(s)	-1.91 ± 2.35	-463.4 ± 5.5	-228.4 ± 17.6	-372.5 ± 3.1	166.63 ± 2.38	-228.4 ± 17.6	114.2 ± 8.8
[CoBr ₂ (TMTU) ₃] _(s)	-61.70 ± 2.07	-396.6 ± 7.5	133 ± 16	-492 ± 2	308.78 ± 2.16	-359 ± 16	120 ± 5
[NiBr ₂ (TMTU) ₂] _(s)	-11.68 ± 2.87	-300.4 ± 5.6	126.2 ± 15.1	-346.5 ± 3.1	176.40 ± 2.90	-220.3 ± 15.4	110.2 ± 7.7
[CuBr ₂ (TMTU) ₂] _(s)	-40.90 ± 1.85	-259.3 ± 3.6	132.4 ± 15.9	-388 ± 2	205.62 ± 1.89	-256 ± 16	128 ± 8
[ZnBr ₂ (TMTU) ₂] _(s)	-41.83 ± 1.28	-447.1 ± 5.2	121.0 ± 14.5	-366.3 ± 2.4	206.55 ± 1.34	-245.3 ± 14.7	122.7 ± 7.4
[CdBr ₂ (TMTU) ₂] _(s)	-19.00 ± 3.10	-131.8 ± 5.6	116.8 ± 14.0	-334.9 ± 3.3	187.72 ± 3.13	-218.1 ± 14.4	109.1 ± 7.2

^a[37]; ^b[38]; ^c[39]; ^d[40].

Table 7. Auxiliary data and enthalpy changes of the complex formation process in the gaseous phase ($\text{kJ}\cdot\text{mol}^{-1}$).

Compound	$\Delta_f H^\circ$	$\Delta_f H^\circ(\text{g})$	$\Delta_n H^\circ$
$\text{Br}_{(\text{g})}^-$	-219.07 ^a		
$\text{Mn}_{(\text{g})}^{2+}$	2522.0 ± 0.1^b		
$\text{Co}_{(\text{g})}^{2+}$	2841.7 ± 3.4^b		
$\text{Ni}_{(\text{g})}^{2+}$	2930.5 ± 1.5^b		
$\text{Cu}_{(\text{g})}^{2+}$	3054.5 ± 2.1^b		
$\text{Zn}_{(\text{g})}^{2+}$	2781.0 ± 0.4^b		
$\text{Cd}_{(\text{g})}^{2+}$	2623.54^a		
$[\text{MnBr}_2(\text{TMTU})_2]_{(\text{g})}$	-319.2 ± 18.2	-228.4 ± 17.6	-2491.3 ± 18.3
$[\text{CoBr}_2(\text{TMTU})_3]_{(\text{g})}$	-265 ± 17	-359 ± 16	-2801 ± 19
$[\text{NiBr}_2(\text{TMTU})_2]_{(\text{g})}$	-174 ± 16	-220.3 ± 15.4	-2755 ± 17
$[\text{CuBr}_2(\text{TMTU})_2]_{(\text{g})}$	-127 ± 17	-256 ± 16	-2832 ± 18
$[\text{ZnBr}_2(\text{TMTU})_2]_{(\text{g})}$	-326.1 ± 15.4	-245.3 ± 14.7	-2757.2 ± 16.1
$[\text{CdBr}_2(\text{TMTU})_2]_{(\text{g})}$	-295 ± 15	-218.1 ± 14.4	-3445 ± 16

^a[38]; ^b[41].

5. Conclusion

Solid state complexes were obtained from the interaction in hot tert-butyl alcohol solution of tetramethylurea with certain divalent transition metal bromides. The complexes decomposed on heating. The dissolution enthalpies were determined for complexes, salts and ligand. By using thermochemical cycles, the energies of the Metal(II)-sulphur coordinated bonds as well as the values of other thermochemical parameters were estimated. The energies of the coordinated bonds have values between 109 and 128 $\text{kJ}\cdot\text{mol}^{-1}$.

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