Trends in Physical Chemistry
Vol. 16, 2016

Original Communication

Metal-sulphur coordinate bond energies in thiourea complexes of certain metal(II) bromides

Pedro Oliver Dunstan[*]

Instituto de Química, Universidade Estadual de Campinas, Campinas, São Paulo, Brazil.

ABSTRACT

The interaction of metal bromides (MBr_2) with thiourea (TU) in solution led to solid compounds. After chemical analyses these compounds could be formulated as $[MBr_2(TU)_n]$, where M is Mn, Co, Ni, Cu, Zn or Cd and n is 2, 3, 4 or 6. Some of the properties of the solid compounds such as melting points were determined and chemical analyses for C, H, N, Br and the metals were performed. Thermogravimetric (TG) analyses and derivative thermogravimetric (DTG) analyses curves and differential scanning calorimetric curves (DSC) of the compounds were obtained. Infrared (IR) and electronic spectroscopic studies of the compounds were carried out. A calorimetric study of the complexes using solution calorimetry was done and thermochemical parameters were determined. Using these parameters the standard enthalpy of the metal-sulphur coordinate bonds were estimated. Also, the enthalpies of the complexes formed in the gaseous state were established.

KEYWORDS: thermodynamic, coordinate bond enthalpies, enthalpies of formation, solution calorimetry

1. INTRODUCTION

Salts of transition and representative elements form complexes with thioamides. In this regard several studies have been carried out. For example J. G. H. Du Prez *et al.* [1] studied the oxovanadium dichloride complexes of thioamides. The complexes are characterized by IR and UV-vis spectra. They also determined the relative energies of the coordinate bonds formed by the ligands. M. Molina *et al.* [2] studied the interaction of thioamides with certain metals. They determined the protonation constant of the complexes and their stabilization constant. V. V. Sibirskaya *et al.* [3] presented a summary of 51 synthesized complexes of platinum metals with primary thioamides. A. J. Aarts *et al.* [4] studied complexes of transition metals dihalides with thioamides. They are characterized by IR and electronic spectra. A. J. Aarts *et al.* [5] prepared palladium dihalides complexes of thioacetamide. They are characterized by IR and electronic spectra. Yu. N. Kukushkin *et al.* [6] prepared complexes of BF_4^- and chloride of palladium(I) and platinum(I) with thioureas. They are characterized by IR spectra and conductance measurements. V. Muresan *et al.* [7] studied the complexes of thioamides with halides of transition metals. They are characterized by IR and UV-vis spectra. J. M. Bret *et al.* [8] studied platinum complexes with thioamides. They studied the reducing power of thioamides. They also prepared mixed/valence Pt(II)/Pt(IV) complexes V. P. Vasil'ev *et al.* [9] studied thiourea complexes of antimony(III) chloride. They determined the enthalpies of formation of the complexes. G. R. Burns *et al.* [10] studied complexes of chromium tri-chloride with thiourea and substituted thiourea. They are characterized by IR and electronic spectra. B. Singh [11] studied the thioamide complexes of oxovanadium(IV). They are characterized by IR and electronic spectra. C. E. Carraher Jr. *et al.* [12] prepared complexes of palladium(II) chloride with polyamines and polythioamides. They are

---

[*]Email id: dunstan@iqm.unicamp.br

characterized by IR and UV-vis spectra. Their biologic activity and their action of inhibition of cell growth were also studied. S. Neagoe *et al.* [13] studied complexes of transition metal with thioamides. They are characterized by IR and UV-vis spectra. H. O. Desseyn [14] studied chelates of thioamides and amides. P. O. Dunstan [15] prepared and characterized complexes of thioamides with arsenic trihalides. A thermal study was also conducted to determine several thermochemical parameters. F. Zalaru *et al.* [16] synthesized complexes of copper(II) chloride with thioamides. They are characterized by IR, UV-vis and EPR spectra. Ligands use N or S as the donor atom. C. Neagoe *et al.* [17] studied tertiary thioamide complexes of transition metals chloride. The IR and UV-vis spectra of the compounds were recorded and their molecular mass measurements were done. Their insecticide action was determined. V. Muresan [18] studied new complexes of transition metals with thioamides. They are characterized by IR, UV-vis and ESR spectra. S. K. Misra *et al.* [19] studied the complex behavior of aromatic thioamides in several transition metal complexes of Ru(II) and Rh(II) halides. Spectroscopic and magnetic measurements were done. L. S. Sbirna *et al.* [20] prepared several complexes of transition metals with bidentate heterocyclic (N, S) ligands. They are characterized by IR and UV-vis spectra. J. Sola *et al.* [21] studied thioamide complexes of silver perchlorate. They determined the crystal structures of the complexes. I. I. Ozturki *et al.* [22] prepared and characterized thioamides complexes of antimony(III) chloride. Crystallographic studies were made to determine the geometry around the Sb(III) ion. S. Nadeem *et al.* [23] studied complexes of palladium(II) bromide with thioamides. IR and NMR spectral studies and x-ray crystallographic studies of the compounds were done. T. Singh *et al.* [24] studied complexes of ruthenium(III) chloride with aromatic thioamides. They are characterized by IR and UV-vis spectra. H. Ajaz *et al.* [25] determined the crystal structure of thioamide complexes of antimony(III) chloride. They are characterized by IR and NMR spectra. The authors determined their x-ray crystallography structures as well. R. Sah *et al.* [26] synthesized and characterized complexes of bidentate cyclic ligands with transition metals(II). N and S are the donor atoms. They are characterized by IR, UV-vis and NMR spectra. M. U. Raja *et al.* [27] prepared palladium dichloride complexes of thioamides. They are characterized by NMR spectra. Their molecular structures were determined by x-ray diffraction. Their action in catalysis was also studied. P. O. Dunstan [28] recently synthesized and characterized complexes of transition metals(II) bromides with tetramethylthiourea. The complexes are characterized by IR and UV-vis spectra. A thermal study was made to determine several thermochemical parameters. The thermodynamic data found in the literature with respect to complexes of thiourea with salts of bivalent transition metals is very poor. It is important to know the thermodynamic properties of this kind of compounds as far as they have applications in catalysis and are also used in the chromatographic separation of the metal ions. A calorimetric study was done to find out the strength of the metal-sulphur coordinate bonds between certain transition metal(II) bromides and thiourea. Based on the data obtained the correlations between the thermodynamic parameters of the complexes were established. The enthalpy of formation of the gaseous-phase complexes was also determined.

2. MATERIALS AND METHODS

2.1. Reagents

Anhydrous metal(II) bromides were prepared and checked for analytical grade. The ligand thiourea (P. A. Aldrich Chemical Company Inc.) (MP = 171-172 °C) was dissolved in methanol prior to use and recrystallized. The solvents used in this study were purified by distillation and stocked in Linde 4Å molecular sieves.

2.2. Experimental procedure

To prepare the complexes a hot solution of metal(II) bromides was mixed with a hot solution of TU in a molar ratio of ¼, using ethanol or tert-butyl alcohol as the solvent. Thus to prepare $[CoBr_2(TU)_6]$, 1.0 g (4.57×10^{-3} mol) of $CoBr_2$ dissolved in 20 mL of hot tert-butyl alcohol and 1.39 g (18.29×10^{-3} mol) of TU dissolved in 20 mL of tert-buthyl alcohol were slowly mixed with constant stirring. The resulting solution was refluxed for about five hours. A green solid was formed which was filtered and washed with petroleum ether followed by vacuum drying for twelve hours. After that the solid was stocked in a desiccator over $CaCl_2$. Analysis of C, H and N contents [29], bromine contents [30] and metal contents [31] confirmed the general formula proposed for the complexes. The infrared (IR) spectra of the complexes were measured in the 4000 to 400 cm^{-1} region using a Bomem MB 100 series FTIR spectrophotometer and a KBr matrix. The spectra of the complexes were obtained in the region 350-2000 nm. A spectrophotometer Vis-NIR with a standard reflectance attachment was used to obtain the spectra of the solid samples. For the thermal study of the complexes a Du Pont 951 analyzer in an argon atmosphere was used and the TG/DTG and DSC curves were obtained. Sample masses between 5.07 and 6.25 mg (TG/DTG) and between 4.00 and 5.07 mg (DSC) were used for obtaining these curves. The mass calibration was done automatically by the apparatus. DSC calibration was done by using metallic indium as a standard (MP = 438.85 K, $\Delta_s^l H^o = 28.4$ J.g^{-1}). For the calorimetric study of the complexes a LKB 8700-1 precision calorimeter was used. The temperature of the calorimetric solvent used for dissolving salts, ligand or complexes was 298.15 ± 0.02 K. The method of measurements and accuracy determination of the equipment were described in previous articles [32, 33]. The number of replicate measurements on each substance was three to seven. The uncertainty intervals are twice the standard deviations.

3. RESULTS

3.1. Characterization of complexes

Solid complexes were obtained as the result of the interaction of MBr_2 (M = Mn, Co, Ni, Cu, Zn or Cd) and TU in solution. On the other hand the interaction of $FeBr_2$ and TU did not yield a complex of definite stoichiometry. Table 1 presents the analytical data and properties of the obtained complexes.

3.2. Infrared studies

The IR spectra of the complexes presents a strong band in the region 723-713 cm^{-1} due to the stretching frequency (ν_{CS}) of the group C=S [15, 24]. When compared with the IR spectra of free TU negative shifts of these frequencies are observed, indicating the coordination of TU through the sulphur atom to the metal(II) bromide [15, 34]. Table 2 shows the main IR bands of the complexes and the ligand. The IR spectrum of the Cu(II) complex is shown in figure 1.

3.3. Thermal studies

The TG curves of solid compounds as revealed from their thermal studies demonstrate the loss in the mass of samples when they are heated. They also show the temperature ranges where these changes occur. The peaks in the DTG curves indicate the thermal processes at the temperatures in which these processes occur. Thus, the TG curve of the Mn(II) complex points out the loss in the mass due to the elimination of all the ligand content in three steps. Elimination of all the bromine content and part of the metal content was observed in the third step of mass loss, together with the elimination of part of the ligand content. A residue was observed that is part of the metal content. In the TG curve of the Co(II) complex the loss of all the ligand content in three steps of

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.**
$[MnBr_2(L)_4]$	54	424-26	l.y.p.	9.25	9.26	3.11	3.33	21.58	21.52	30.78	30.75	10.58	10.56
$[CoBr_2(L)_6]$	32	378-79	g.p.	10.67	11.28	3.58	3.61	24.88	24.50	23.66	23.61	8.72	8.69
$[NiBr_2(L)_3]$	98	381-83	y.p.	8.06	8.51	2.71	2.84	18.81	18.95	35.76	35.56	13.14	13.07
$[CuBr_2(L)_4]$	30	447-48	w.p.	9.10	9.79	3.06	3.16	21.23	21.95	30.28	30.24	12.04	12.01
$[ZnBr_2(L)_2]$	72	431-32	w.p.	6.36	6.69	2.14	2.16	14.84	14.73	42.34	42.30	17.32	17.28
$[CdBr_2(L)_2]$	58	463-65	w.p.	5.66	5.97	1.90	1.94	13.20	13.11	37.27	37.23	26.48	26.42

[a]Melting with decomposition. [b]Key: y., yellow; g., green; w., white; l., light; p., powder.

loss of mass was observed. Part of the bromine content is lost together with part of the ligand content in the third step of mass loss. In a fourth step a part of the bromine content is lost. A residue that is part of the bromine content plus the metal content was observed. In the TG curve of the Ni(II) complex the loss of all the ligand content in two steps of mass loss was observed. Part of the bromine content is lost in the second step together with part of the ligand content. The rest of the bromine content is lost in the following three more steps of mass loss, leaving a residue that is the metal content. In the TG curve of the Cu(II) complex the loss of all the ligand content plus part of the bromine content in the first step of mass loss was observed. The rest of the bromine content is lost in three more steps of mass loss leaving a residue that is the metal content. The TG curve of Zn(II) complex points out the loss of all the ligand content in two steps of mass loss. Part of the bromine content is lost in a third step of mass loss. The rest of the bromine content together with part of the metal content is lost in a fourth step. A residue is observed that is part of the metal content. The TG curve of the Cd(II) complex shows the loss of all the ligand content in two steps of mass loss. The bromine content is lost in the second step together with part of the ligand content. Part of the metal content is lost in a third step of mass loss. A residue is observed that is part of the metal content. The TG curve of the Co(II) complex is shown in figure 2. The DSC curves of compounds show the temperatures and the enthalpy values of the thermal events that result when samples are heated. The DSC curves of the complexes are consistent with the TG data. They show endothermic peaks that result from the partial elimination of ligand content, or the partial elimination of bromine content together with part of the ligand content, or even the elimination of all the ligand content together with part of the bromine content. The DSC curves also show exothermic peaks for the Mn(II) and Ni(II) complexes.

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

Compound	Assigment[a] $\nu_{(CS)}$	$\nu_{(CN)}$
TU	1413 s	1474 s
$[MnBr_2(TU)_4]$	1392 s	1498 m
$[CoBr_2(TU)_6]$	1381 sh	1499 m
$[NiBr_2(TU)_3]$	1396 s	1476 m
$[CuBr_2(TU)_4]$	1389 s	1477 m
$[ZnBr_2(TU)_2]$	1395 s	1489 m
$[CdBr_2(TU)_2]$	1388 s	1490 m

[a]ν, stretching. Intensity of bands: s, strong; m. medium; sh, shoulder.

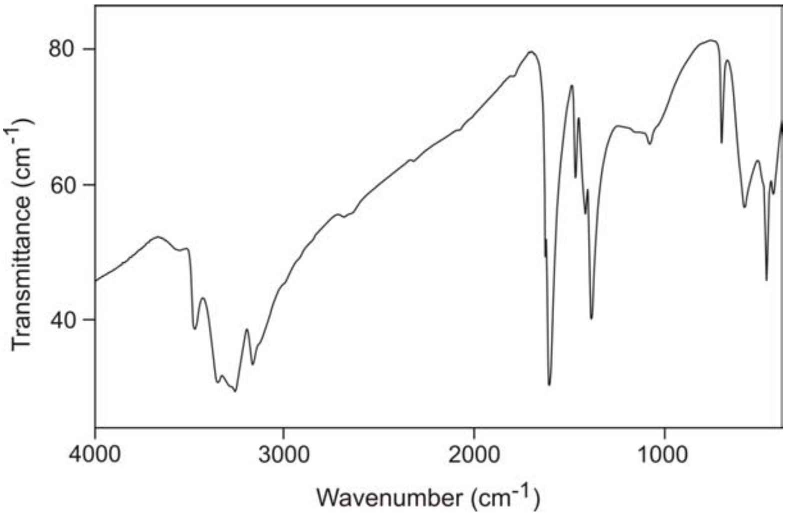

Figure 1. Infrared spectrum of the complex $[CuBr_2(TU)_4]$.

These peaks are due to the decomposition of the complexes. The DSC curve of Co(II) complex is shown in figure 3. Table 3 shows the thermoanalytical data of the complexes.

3.4. Electronic spectra

The ligand field parameters for the Ni(II) complex in the present study were calculated according to Reedijk *et al.* [35] and Lever [36]. The values of the crystal field parameters indicate a pseudo-tetrahedral Ni(II) complex with one bromide ion and three sulfhur atoms from three TU molecules in the inner coordination sphere surrounding the Ni(II) ion. The bands observed for Co(II) complex [36] indicates that the ion Co(II) is pseudo-octahedral with six sulphur atoms from six TU molecules surrounding the Co(II) ion. The broad band observed for the Cu(II) ions indicates, according to Bolster [37], that the Cu(II) ion is pseudo-octahedral with two bromide ions and four sulphur atoms from four TU molecules surrounding the Cu(II) ion. The band observed for the Mn(II)

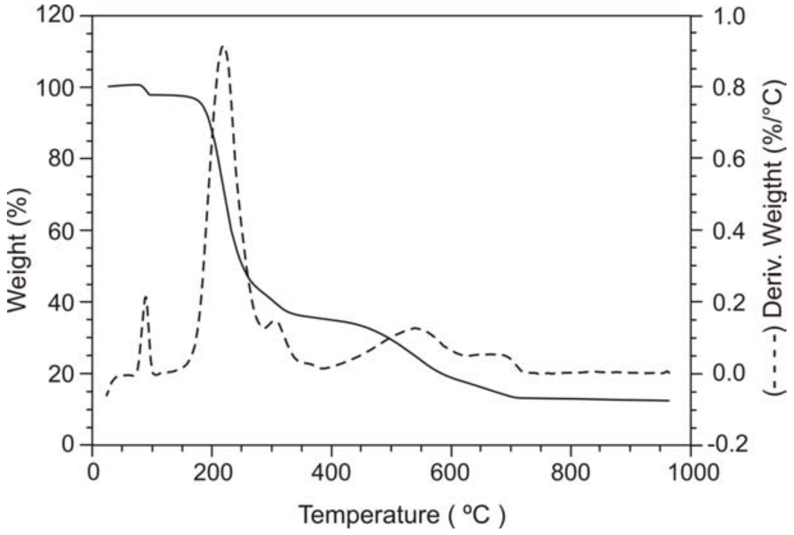

Figure 2. TG/DTG curve of the complex [CoBr$_2$(TU)$_6$].

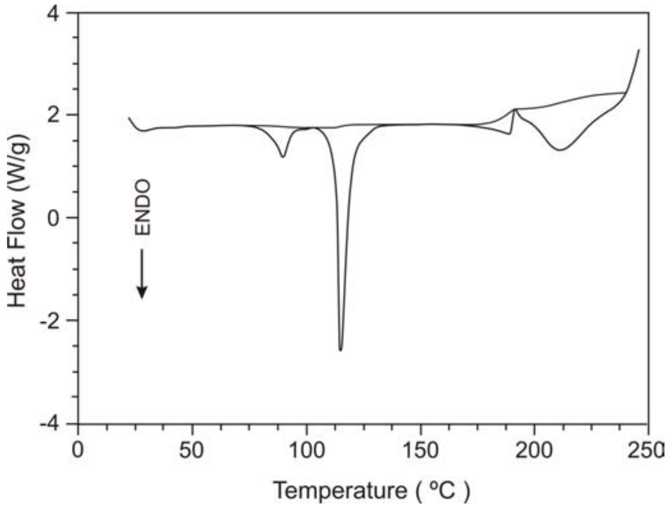

Figure 3. DSC curve of the complex [CoBr$_2$(TU)$_6$].

Table 3. Thermal analysis of the compounds.

Compound	**Apparent MP/K**	**Mass**		**TG temperature range/K**	**Species lost**	**DSC peak temperature**	**ΔH^{o}/kJ·mol^{-1}**
		Calcd.	**Obs.**				
$[MnBr_2(TU)_4]$	424-426	2.93	2.81	352-394	-0.2TU	330	3.19
		52.78	53.40	394-527	-3.6TU	413	54.79
		39.53	39.89	527-1008	-0.2TU-2Br-0.55Mn	433	14.91
			4.76[a]			459	10.74
						499	-52.96
$[CoBr_2(TU)_6]$	378-379	2.25	2.29	350-367	-0.2TU	356	18.85
		61.99	62.52	464-529	-5.5TU	386	101.79
		18.76	18.22	529-853	-0.3TU-1.3Br	447	12.85
		4.73	4.74	853-979	-0.4Br	464	99.77
			12.23[a]				
$[NiBr_2(TU)_3]$	381-383	1.76	1.84	361-381	-0.1TU	280	0.76
		56.53	56.41	469-547	-2.9TU-0.4Br	369	11.79
		19.67	19.79	547-886	-1.1Br	441	2.44
		2.56	2.54	886-938	-0.15Br	464	58.36
		0.80	0.79	938-1240	-0.045Br	477	-74.81
			18.63[a]				
$[CuBr_2(TU)_4]$	447-448	65.25	65.49	474-545	-4TU-0.5Br	443	73.95
		6.06	6.14	545-799	-0.4Br	466	4.99
		13.63	13.62	799-951	-0.9Br		
		3.03	2.48	1160-1221	-0.2Br		
			12.27[a]				
$[ZnBr_2(TU)_2]$	431-432	30.48	30.48	484-586	-1.5TU	430	44.88
		10.09	11.21	586-621	-0.5TU	477	29.62
		38.11	39.34	621-918	-1.8Br		
		10.30	10.33	918-948	-0.2Br-0.35Zn		
			8.64[a]				
$[CuBr_2(TU)_2]$	463-465	26.90	27.16	480-523	-1.5TU	343	0.98
		66.49	66.83	523-868	-0.5TU-2Br-0.75Cd	470	56.79
		2.65	2.30	1210-1217	-0.1Cd	482	18.46
			3.71[a]				

[a]Residue at 1243 K.

complex indicates [37] that the Mn(II) ion is pseudo-octahedral with two bromide ions and four Sulphur atoms from four TU molecules surrounding the Mn(II) ion. Table 4 presents the band maxima assignments and calculated ligand field parameters of the complexes.

3.5. Calorimetric measurements

The standard enthalpies of reaction ($\Delta_r H^o$) can be determined from reaction (1):

$$MBr_{2(s)} + n\ TU_{(s)} \rightarrow [MBr_2(TU)_n]_{(s)}; \quad \Delta_r H^o \qquad (1)$$

These standard enthalpies of reaction were obtained from the standard enthalpy changes of reactions (2)-(5) in solution [38]:

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

$$n\ TU_{(s)} + \text{solution A} \rightarrow \text{solution B}; \quad \Delta_2 H^o \qquad (3)$$

$$[MBr_2(TU)_n]_{(s)} + \text{calorimetric solvent} \rightarrow \text{solution C}; \quad \Delta_3 H^o \qquad (4)$$

$$\text{Solution B} \rightarrow \text{solution C}; \quad \Delta_4 H^o \qquad (5)$$

The application of the Hess's law to the series of reactions (2)-(5) gives $\Delta_r H^o$.

Thus $\Delta_r H^o = \Delta_1 H^o + \Delta_2 H^o - \Delta_3 H^o$ since the final B and C solutions are equivalent and $\Delta_4 H^o = 0$. Table 5 gives the values for the enthalpies of dissolution of MBr_2 ($\Delta_1 H^o$), for the enthalpies of dissolution of TU into the solution of MBr_2 ($\Delta_2 H^o$) and that of the complexes ($\Delta_3 H^o$). Uncertainty intervals given in this table are twice the standard deviation of the mean of 3 to 7 replicate measurements.

4. DISCUSSION

The standard enthalpy of formation ($\Delta_f H^o$) of the complexes can be determined from the standard enthalpy of formation of the metal(II) bromides and that of TU and from the ($\Delta_r H^o$) values obtained for reaction (1): $\Delta_f H^o(\text{complex}_{(s)}) = \Delta_r H^o + \Delta_f H^o(MBr_{2(s)}) + n\ \Delta_f H^o(TU_{(s)})$.

The standard enthalpies of reactions (6) and (7), ($\Delta_D H^o$) and ($\Delta_M H^o$), respectively were also determined.

$$[MBr_2(TU)_n]_{(s)} \rightarrow MBr_{2(s)} + n\ TU_{(g)}; \quad \Delta_D H^o \qquad (6)$$

$$MBr_{2(g)} + n\ TU_{(g)} \rightarrow [MBr_2(TU)_n]_{(s)}; \quad \Delta_M H^o \qquad (7)$$

From equations (6) and (7) the following can be derived: $\Delta_D H^o = -\ \Delta_r H^o + n\ \Delta_s^g H^o(TU_{(s)})$ and $\Delta_M H^o = -\ \Delta_D H^o - \Delta_s^g H^o\ (MBr_{2(s)})$. The standard enthalpy of interaction of metal(II) bromides with TU in the gaseous phase ($\Delta_r H^o(g)$),

$$MBr_{2(g)} + n\ TU_{(g)} \rightarrow [MBr_2(TU)_n]_{(g)}; \quad \Delta_r H^o(g) \qquad (8)$$

where $\Delta_r H^o(g) = -\ \Delta_s^g H^o(MBr_{2(s)}) - n\ \Delta_s^g H^o(TU_{(s)}) + \Delta_r H^o + \Delta_s^g H^o(\text{complex})$, can be used to calculate the standard enthalpy of the metal(II)-sulphur bond ($D_{(M-S)} = -(\Delta_r H^o(g))/n.$), if the values of the standard enthalpy of sublimation of each complex is known. As the complexes decomposed on heating; the enthalpies of sublimation of the complexes were estimated [39]. Table 6 presents the values obtained for all these enthalpies. The enthalpies of

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

Compound	**Band maxima (x 10^3 cm^{-1})**							**Interligand + charge transfer (x 10^3 cm^{-1})**
	d-d							
$[MnBr_2(TU)_4]$	23.42							285.69
$[CuBr_2(TU)_4]$	9.47							
	ν_1	ν_2	ν_3	Dq (cm^{-1})	B	Dq/B	β^+	
$[CoBr_2(TU)_6]$	7.59^a	15.65^b	22.32^c	806	209	3.859	0.215	28.59, 29.99
$[NiBr_2(TU)_3]$		8.06^d	12.82^e	295	370	0.797	0.359	

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

Table 5. Enthalpies of dissolution at 298.15K.

Compound	**Calorimetric solvent**[a]	**Number of experiments**	**i**	**ΔH^o (kJ·mol^{-1})**
$MnBr_{2(s)}$	1.2 M HCl	5	1	-43.96 ± 1.73
$TU_{(s)}$	4:1 $MnBr_2$-1.2 M HCl	4	2	91.07 ± 4.65
$[MnBr_2(TU)_4]_{(s)}$	1.2 M HCl	4	3	66.23 ± 3.42
$CoBr_{2(s)}$	1.2 M HCl	6	1	-69.23 ± 0.80
$TU_{(s)}$	6:1 $CoBr_2$-1.2 M HCl	4	2	137.16 ± 2.29
$[CoBr_2(TU)_6]_{(s)}$	1.2 M HCl	4	3	82.32 ± 3.46
$NiBr_{2(s)}$	1.2 M HCl	7	1	-58.03 ± 0.62
$TU_{(s)}$	3:1 $NiBr_2$-1.2 M HCl	4	2	58.63 ± 2.34
$[NiBr_2(TU)_3]_{(s)}$	1.2 M HCl	4	3	34.60 ± 1.94
$CuBr_{2(s)}$	10% EA-25% ET-65% H_2O	3	1	-42.39 ± 1.90
$TU_{(s)}$	4:1 $CuBr_2$-10% EA-25% ET-65% H_2O	4	2	61.21 ± 6.71
$[CuBr_2(TU)_4]_{(s)}$	10% EA-25% ET-65% H_2O	4	3	60.43 ± 2.89
$ZnBr_{2(s)}$	1.2 M HCl	7	1	-42.50 ± 0.50
$TU_{(s)}$	2:1 $ZnBr_2$-1.2 M HCl	3	2	39.11 ± 0.79
$[ZnBr_2(TU)_2]_{(s)}$	1.2 M HCl	3	3	59.26 ± 0.46
$CdBr_{2(s)}$	10% EA-25% ET-65% H_2O	5	1	-34.47 ± 1.08
$TU_{(s)}$	2:1 $CdBr_2$-10% EA-25% ET-65% H_2O	4	2	40.88 ± 0.48
$[CdBr_2(TU)_2]_{(s)}$	10% EA-25% ET-65% H_2O	5	3	29.78 ± 1.85

[a] 1.2 M HCl, aqueous 1.2 M HCl; EA, triethanolamine; ET, ethanol.

Table 6. Summary of the thermochemical results (kJ·mol^{-1}) for the compounds.

Compound	**$\Delta_r H^o$**	**$\Delta_f H^o$**	**$\Delta_s^g H^o$**	**$\Delta_M H^o$**	**$\Delta_D H^o$**	**$\Delta_r H^o(g)$**	**$D_{(M-S)}$**
$MnBr_{2(S)}$		-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]				
$TU_{(s)}$		-89.12 ± 0.12[d]	93.7 ± 4.7[d]				
$[MnBr_2(TU)_4]_{(s)}$	-19.12 ± 6.03	-760.5 ± 6.4	149.8 ± 18.0	-599.8 ± 19.8	393.9 ± 19.7	-450.0 ± 26.8	112.5 ± 6.7
$[CoBr_2(TU)_6]_{(s)}$	-14.99 ± 4.23	-770.6 ± 4.7	138 ± 17	-760 ± 29	577.2 ± 6.3	-622 ± 33	138 ± 17

Table 6 continued..

Compound	Δ_rH^o	Δ_fH^o	$\Delta_s^gH^o$	Δ_MH^o	Δ_DH^o	$\Delta_rH^o(g)$	$D_{(M-S)}$
$[NiBr_2(TU)_3]_{(s)}$	-34.00 ± 3.10	-89.26 ± 3.28	131.9 ± 15.8	-485.2 ± 14.5	315.1 ± 14.4	-353.3 ± 21.4	117.8 ± 7.1
$[CuBr_2(TU)_4]_{(s)}$	-41.61 ± 7.55	-539.9 ± 7.8	138.1 ± 16.6	-598.81 ± 20.28	416.41 ± 20.26	-460.7 ± 25.8	115.2 ± 6.5
$[ZnBr_2(TU)_2]_{(s)}$	-62.65 ± 1.04	-569.54 ± 2.27	126.7 ± 15.2	-409.8 ± 9.7	250.1 ± 4.8	-283.1 ± 18.0	141.6 ± 9.0
$[CdBr_2(TU)_2]_{(s)}$	-23.37 ± 2.20	-517.8 ± 2.4	122.5 ± 14.7	-362.0 ± 9.7	210.8 ± 9.7	-239.5 ± 17.6	119.8 ± 8.8

References where the data can be found: [a][40]; [b][41]; [c][42]; [d][43].

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

Compound	Δ_rH^o	$\Delta_fH^o(g)$	$\Delta_{fl}H^o$
$Br^-_{(g)}$	-219.07[a]		
$Mn^{2+}_{(g)}$	2522.0 ± 0.1[b]		
$Co^{2+}_{(g)}$	2841.7 ± 3.4[b]		
$Ni^{2+}_{(g)}$	2930.5 ± 1.5[b]		
$Cu^{2+}_{(g)}$	3054.5 ± 2.1[b]		
$Zn^{2+}_{(g)}$	2781.0 ± 0.4[b]		
$Cd^{2+}_{(g)}$	2623.54[a]		
$[MnBr_2(TU)_4]_{(s)}$	-610.6 ± 19.0	-450.0 ± 26.8	-2712.9 ± 26.8
$[CoBr_2(TU)_6]_{(s)}$	-632 ± 43	-622 ± 33	-3063 ± 52
$[NiBr_2(TU)_3]_{(s)}$	-382 ± 26	-353.3 ± 21.4	-2888 ± 26
$[CuBr_2(TU)_4]_{(s)}$	-401.7 ± 32.0	-460.7 ± 25.8	-3036.6 ± 37.2
$[ZnBr_2(TU)_2]_{(s)}$	-442.9 ± 20.3	-283.1 ± 18.0	-2795.0 ± 9.8
$[CdBr_2(TU)_2]_{(s)}$	-395 ± 20	-239.5 ± 17.6	-2590 ± 22

References where the data can be found: [a][41]; [b][44].

formation of the complexes in the gaseous phase, according to the equation (9):

$$M_{(g)}^{2+} + 2\,Br_{(g)}^- + n\,TU_{(g)} \rightarrow [MBr_2(TU)_n]_{(g)};\quad \Delta_{fl}H^o(g) \qquad (9)$$

are equal to: $\Delta_{fl}H^o(g) = \Delta_fH^o(complex_{(g)}) - \Delta_fH^o(M_{(g)}^{2+}) - 2\,\Delta_fH^o(Br_{(g)}^-) - n\,\Delta_fH^o(TU_{(g)})$. Table 7 shows the values obtained for these enthalpies. The acidity order of the metal(II) bromides obtained based on the Δ_rH^o values for the complexes of the same stoichiometry is: Zn(II) > Cd(II) and Cu(II) > Mn(II). The order is the same when using the $D_{(M-S)}$ values.

5. CONCLUSION

In complexes formed by the ligands (Lewis bases) thiourea (TU) and tetrametylthiourea (TMTU) [28] with the same salt (Lewis salt) and with the same stoichiometry, the Δ_rH^o and $D_{(M-S)}$ values indicate that the M-S bond is stronger, as we go in the sequence: TMTU<TU ($ZnBr_2$ and $CdBr_2$ complexes). The stronger bond is formed by the stronger base. On the contrary, in complexes formed by the same ligand with the same stoichiometry but different salt, the M-S bond is stronger in the sequence: $CdBr_2<CuBr_2<ZnBr_2$ (TMTU complexes). The stronger bond is formed by the stronger acid. This means that $ZnBr_2$ is a stronger acid than $CuBr_2$ and $CdBr_2$. Also $MnBr_2< CuBr_2$ (TU complexes) means that $CuBr_2$ is a stronger acid than $MnBr_2$. The substitution of four hydrogen atoms in TU with four methyl groups in TMTU leads to a weaker M-S coordinated bond. The energies of the M-S coordinate bonds of TU complexes have values between 112 and 141 kJ·mol^{-1}.

CONFLICT OF INTEREST STATEMENT

There are no conflicts of interest.

REFERENCES

1. Du Preez, J. G. H. and Gibson, M. L. 1970, J. South Afr. Chem. Inst., 23, 184.
2. Molina, M., Del'acqua, A., Melios, C. V., Azevedo, F. A. and Trabuco, E. 1977, Eclé. Quím., 2, 87.
3. Sibirskaya, V. V. and Kukushkin, Y. N. 1978, Koord. Khim., 4, 963.
4. Aarts, A. J., Desseyn, H. O. and Herman, M. A. 1976, Bull. Soc. Chim. Bel., 85, 854. http://dx.doi.org/10.1002/bscb.19760851103
5. Aarts, A. J., Desseyn, H. O. and Herman, M. A. 1978, Trans. Met. Chem., 3, 144. http://dx.doi.org/10.1007/BF01393531
6. Kukushkin, Y. N., Vorob'ev-Desyatovsku, N. V., Sibirskaya, V. V. and Stmkov, V. V. 1980, Zhur. Obs. Khim., 50, 107.
7. Muresan, V. and Muresan N. 1980, Thio Complex Compound Chemistry. Part VIII. Anal. Univ. Crai., 8, 97.
8. Bret, J. M., Castan, P. and Laurent, J. P. 1983, Trans. Met. Chem., 8, 218-221. http://dx.doi.org/10.1007/BF00620694
9. Vasil'ev, V. P., Raskova, O. G., Shorokhova, V. I. and Katnovtseva, A. V. 1984, Russ. J. Inorg. Chem., 29, 1615.
10. Burns, G. R., DeRoo, C. R., Hall, D. W. and Oliver, A. R. 1987, Inorg. Chim. Acta, 130, 13. http://dx.doi.org/10.1016/S0020-1693(00)85921-6
11. Singh, B. 1987, Ind. Jour. Chem. Sec. A, 26, 350.
12. Carraher Jr., C. E., Cen, W. and Hess, G. G. 1988, Poly. Mat. Sci. Eng., 58, 557.
13. Neagoe, S., Antonescu, L., Negoiu, M. Negoe, V., Negoiuand, D. and Cecasov, C. 1989, Rev. Roum. Chim., 34, 848.
14. Desseyn, H. O. 1989, Pur. App. Chem., 61, 867. http://dx.doi.org/10.1351/pac198961050867
15. Dunstan, P. O. and Dos Santos, L. C. R. 1989, Therm. Acta, 156, 163. http://dx.doi.org/10.1016/0040-6031(89)87182-5
16. Zalaru, F., Cercasov, C. Meghea, A., Zalarau, C. and Jalen, C. 1991, Rev. Roum. Chem., 36, 1279.
17. Neagoe, C., Neagoe, S., Negaoe, O., Cercasov, C. and Lapadatu, C. 1999, Rom. Arc. Mic. Immu., 58, 209.
18. Muresan, V., Sbirna, L. S., Sbirna, S., Lepadatu, C. I. and Muresan, N. 2001, Acta Chim. Slov., 48, 439.
19. Misra, S. K. and Tewari, U. C. 2002, Trans. Met. Chem., 27, 120. http://dx.doi.org/10.1023/A:1013473621826
20. Sbirna, L. S., Muresan, V., Sbirna, S., Muresan, N. and Lepadatu, C. I. 2004, J. Ind. Chem. Soc., 81, 150.
21. Sola, J., Lopez, A., Coxall, R. A. and Clegy, W. 2004, J. Inorg. Chem., 24, 4871.
22. Ozturki, I. I., Hadjikakou, S. K., Hadjiliardis, N., Kourkoumelis, N., Kubicki, M., Tasiopolulosu, A. J., Scleiman, H., Barsan, M. M., Butler, I. S. and Balzarini, J. 2009, Inorg. Chem., 48, 2233. http://dx.doi.org/10.1021/ic8019205
23. Nadeem, S., Rauf, M. K., Bolte, M., Ahmad, S., Tirmizi, S. A., Asna, M. and Hamees, A. 2010, Trans. Met. Chem., 35, 555. http://dx.doi.org/10.1007/s11243-010-9363-0
24. Singh, T. and Sing, K. K. 2010, Or. J. Chem., 26, 1171.
25. Ajaz, H., Hussain, S., Alfat, M., Stoeckli-Evans, H., Isab, A. A., Mahmood, R., Alfaf, S. and Ahmad, S. 2011, Chin. J. Chem., 29, 254. http://dx.doi.org/10.1002/cjoc.201190074
26. Sah, R., Kumari, S. and Kumar, A. 2011, J. Chem., 23, 3563.
27. Raja, M. U., Ramesh, R. and Liu, Y. 2011, Tetr. Lett., 52, 5427. http://dx.doi.org/10.1016/j.tetlet.2011.07.080

28. Dunstan, P. O. 2015, Open J. Phys. Chem., 5, 9. http://dx.doi.org/10.4236/ojpc.2015.51002
29. Niederland, J. B. and Sozzi, J. A. 1958, Microanálisis Elemental Orgánico, Methopress, Buenos Aires.
30. Kolthoff, I. M. and Sandall, E. B. 1956, Tratado de Química Analítica Cuantitativa. 3ª Edition, Nigar, Buenos Aires.
31. Flaschka, H. H. 1964, EDTA Titrations: An Introduction to Theory and Practice. 2nd Edition, Pergamon Press, London.
32. Dunstan, P. O. 1999, J. Chem. Eng. Data, 44, 243. http://dx.doi.org/10.1021/je980113m
33. Herington, E. F. 1991, Pure Appl. Chem., 24, 261.
34. Kharitonov, Yu. Ya., Brega, V. D., Ablov, A. V. and Proskina, N. N. 1974, Russ. J. Inorg. Chem., 19, 1187.
35. Reedijk, J., van Leeuwem, P. W. N. M. and Groenveld, W. L. 1968, Recueil Trava. Chimi. Pays-Bas, 87, 129. http://dx.doi.org/10.1002/recl.19680870203
36. Lever, A. B. P. 1968, J. Chem. Edu., 45, 711. http://dx.doi.org/10.1021/ed045p711
37. Bolster, M. W. G. 1972, The Coordination Chemistry of Amino-Phosphinoxide and Related Compounds. Thesis, Leiden University, Leiden.
38. Dunstan, P. O. and Majeed Khan, A. 2014, J. Chem. Eng. Chem. Res., 1, 238.
39. Sovast'yamova, T. N. and Suvorov, A. V. 1999, Russ. J. Coord. Chem., 25, 679.
40. Dunstan, P. O. 2004, Therm. Acta, 409, 19. http://dx.doi.org/10.1016/S0040-6031(03)00333-2
41. Wagman, D. D., Evans, W. H., Parker, V. B., Schumm, R. H., Hallow, I. S., Churney, M. and Nuttall, R. L. 1982, J. Phys. Chem. Ref. Data, 2, 50.
42. Kubaschewiski, O., Evans, E. L. and Alcock, C. B. 1967, Metallurgical Thermochemistry, 4th Edition, Pergamon, London.
43. Dunstan, P. O. 2009, J. Ther. Anal. Cal., 97, 755. http://dx.doi.org/10.1007/s10973-009-0335-6
44. Skinner, H. A. and Pilcher, G. 1963, Quar. Rev. Chem. Soc., 17, 264. http://dx.doi.org/10.1039/qr9631700264