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Enthalpies of Formation of Bis(thiourea) Complexes of Cobalt, Zinc, Cadmium, Mercury, and Silver Chlorides

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The standard enthalpies of formation of crystalline complexes of thiourea with metal chlorides of the types $[M^{II}tu_2Cl_2]$ (M^{II} = Co, Zn, Cd, Hg) and $[M^{I}tu_2Cl]$ (M^{I} = Ag) have been measured by reaction calorimetry at 298.15 K. Enthalpies of sublimation have also been measured, or estimated in the case of $[Hgtu_2Cl_2]$, leading to values for the enthalpies of formation of the gaseous complexes. The mean metal-sulfur coordinate bond dissociation energies range from 179 kJ mol^{-1} for the cobalt complex to 104 kJ mol^{-1} for the mercury complex.

Introduction

Metal complexes with thiourea [$SC(NH_2)_2$ = tu] have been extensively studied by spectroscopic and X-ray methods. A wide variety of structures has been observed in which the thiourea is almost always bonded through the sulfur atom. A small amount of quantitative information on the strengths of the metal–ligand bond has been reported. An earlier thermochemical study (*1*) on the octahedral $[M^{II}tu_4Cl_2]$ complexes of the first transition series metals showed that the mean metal–sulfur bond energies lie in the range 125–148 kJ mol^{-1}, noticeably weaker than M–O and M–N bonds in comparable H_2O and NH_3 complexes. Similar observations were also reported (*2*) for complexes of substituted thioureas. Significant ligand field effects were apparent in both these series of complexes.

In this paper calorimetric measurements are reported for the first time on a number of crystalline bis(thiourea) complexes of known structures, leading to values for their enthalpies of formation. The complexes are $[M^{II}tu_2Cl_2]$ (M^{II} = Co, Zn, Cd, Hg) and $[M^{I}tu_2Cl]$ (M^{I} = Ag). Less precise data are also reported for the complexes in the gaseous state.

Experimental Section

Materials. Analytical grade materials were used throughout. The synthesis and purification of the complexes followed procedures which were well documented in the literature. The complexes of $ZnCl_2$ and $CdCl_2$ were made by the method of Rosenheim and Meyer (*3*) and then recrystallized from aqueous ethanol (20 vol % H_2O). The mercury complex was made as described by Aucken (*4*), $[Agtu_2Cl]$ by the method of Nardelli et al. (*5*), and $[Cotu_2Cl_2]$ by the method of Cotton et al. (*6*). Comparison of melting temperatures with literature values (Table I) shows good agreement, there being no evidence in the DSC output of the presence of any free ligand or any other impurity in the complexes. The mercury complex was found to decompose at 500 K before melting. Aucken (*4*) reported melting with decomposition at 523 K. The closeness of the melting temperatures of thiourea and the silver complex might possibly have obscured the presence of free ligand. In this case the infrared spectrum was recorded over the wavelength range 2.5–25.0 μm and compared with the spectrum reported in the literature for thiourea (*1*). No evidence of any impurity was observed. The spectrum of the silver complex does not appear to have been reported in the literature. Analyses of the complexes in terms of mass percent nitrogen content, with calculated values in parentheses were $[Cotu_2Cl_2]$ 19.7% (19.8 %), $[Zntu_2Cl_2]$ 19.1 % (19.4 %), $[Cdtu_2Cl_2]$ 16.5 % (16.7 %), $[Hgtu_2Cl_2]$ 13.0 % (13.2 %), and $[Agtu_2Cl]$ 18.3 % (18.9 %).

Table I. Melting Temperatures, T_{fus}, Decomposition Temperatures, T_{dec}, and Enthalpies of Sublimation, Δ_s^gH, of Complexes and Thiourea

	T_{fus}/K				
compd	found	lit.	T_{dec}/K	Δ_s^gH/kJ mol^{-1}	temp/K
$[Cotu_2Cl_2]$	422	421 (*6*)	500	127.2 ± 6.3	386–405
$[Zntu_2Cl_2]$	433	431 (*12*)	492	97.9 ± 4.9	391–409
$[Cdtu_2Cl_2]$	484	483 (*12*)	502	115.1 ± 5.8	400–414
$[Agtu_2Cl]$	452	448 (*5*)	475	151.9 ± 7.6	396–418
$[Hgtu_2Cl_2]$			500	132^a ± 26	
tu	455	455 (*9*)		93.7 ± 4.7	348–382
tu^c				95.2^b ± 4.8	298.15

^{a} Estimated value with error ±20%. ^{b} Corrected to 298.15 K by using heat capacity data (*13*, *14*). ^{c} Measured Δ_s^lH = 15.28 ± 0.30 kJ mol^{-1} by DSC at 455 K.

Enthalpies of Reaction. These were measured in a L.K.B 8700-1 calorimeter by standard procedures (*7*). The temperature in the calorimeter was measured with a thermistor, and the instrument was calibrated electrically. A check on the efficacy of the calorimetric procedure was made using the IUPAC recommended (*8*) test reaction of tris(hydroxymethyl)aminomethane with 0.1 M hydrochloric acid. Agreement to within 0.3% was obtained, although a slightly lower concentration of THAM (≈4 g dm^{-3}) than recommended was used. The materials were sealed into glass ampules and weighed on a microbalance using a set of weights calibrated at the National Physical Laboratory. Corrections were made for buoyancy in air by using the densities given in the literature cited earlier for the complexes and in ref *9* for the other materials. Values of ΔH refer to the isothermal reaction at 298.15 K under atmospheric pressure, the latter being sufficiently close to the IUPAC recommended (*10*) reference pressure of 1 bar to have negligible effect on the enthalpies.

Melting Temperatures, Decomposition Temperatures, and Enthalpies of Sublimation. Melting and decomposition temperatures refer to the onset of these changes as detected by a Perkin-Elmer differential scanning calorimeter (Type DSC-1), with the samples placed in a continuously swept nitrogen atmosphere. Enthalpies of sublimation were measured (*11*) by a duPont 950 thermogravimetric analyzer over a 20–30 K temperature range, at temperatures below the onset of melting and decomposition. A check for thermal decomposition was made by collecting samples of sublimate and recording the DSC trace. For the silver complex the infrared spectrum was also recorded. No evidence of decomposition was seen. A consistent result for enthalpy of sublimination could not be obtained for $[Hgtu_2Cl_2]$, presumably due to decomposition.

Uncertainties. Uncertainty intervals given in Table II are twice the standard deviations of the means of about four or five replicate measurements on each compound. An uncertainty of ±5% was assigned (*11*) to the enthalpies of sublimation. Combined errors were calculated from the root of the sum of the squares of the component errors.

Results

The crystalline complexes, except for $[Agtu_2Cl]$ and $[Hgtu_2Cl_2]$, react (1) at an adequate rate with an excess of

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Table II. Enthalpy Changes, at 298.15 K, for Reactions 1–12

compd	reaction	ΔH/kJ mol^{-1}
[$\mathrm{Cotu_2Cl_2}$]	1	6.745 ± 0.067
[$\mathrm{Zntu_2Cl_2}$]	1	40.60 ± 0.13
[$\mathrm{Cdtu_2Cl_2}$]	1	56.58 ± 2.2
thiourea	2	43.547 ± 0.092
$\mathrm{CoCl_2}$	3	−72.74 ± 0.84
$\mathrm{ZnCl_2}$	3	−46.02 ± 0.42
$\mathrm{CdCl_2}$	3	−23.68 ± 0.13
[$\mathrm{Cotu_2Cl_2}$]	4	−35.94 ± 0.85
[$\mathrm{Zntu_2Cl_2}$]	4	−43.08 ± 0.45
[$\mathrm{Cdtu_2Cl_2}$]	4	−36.71 ± 2.2
[$\mathrm{Agtu_2Cl_2}$]	5	42.2 ± 1.7
thiourea	6	38.024 ± 0.079
AgCl	7	−29.08 ± 0.20
[$\mathrm{Agtu_2Cl_2}$]	8	−33.3 ± 1.7
[$\mathrm{Hgtu_2Cl_2}$]	9	40.13 ± 0.67
thiourea	10	38.024 ± 0.079
$\mathrm{HgCl_2}$	11	−63.5 ± 2.0
[$\mathrm{Hgtu_2Cl_2}$]	12	−65.6 ± 2.2

aqueous hydrochloric acid to give the aqueous metal chloride and protonated thiourea. Enthalpy changes for this reaction (1) were measured and are reported in Table II. Also in Table II are values of the enthalpy change for reaction 2 of crystalline thiourea with hydrochloric acid containing metal chloride, and of the enthalpy of solution (3) of the crystalline metal chloride in hydrochloric acid. The enthalpy change for the formation of the crystalline complex from crystalline metal chloride and crystalline thiourea, reaction 4, was found from $\Delta H(4) = \Delta H(2) + \Delta H(3) - \Delta H(1)$.

$$[\mathrm{Mtu_2Cl_2}](\mathrm{cr}) + 87\ \mathrm{HCl}(\mathrm{aq},4640\mathrm{H_2O}) = \mathrm{MCl_2}(\mathrm{aq,HCl}) + 2\mathrm{tu}(\mathrm{aq,HCl}) \tag{1}$$

$$2\mathrm{tu}(\mathrm{cr}) + 87\mathrm{HCl}(\mathrm{aq},4640\mathrm{H_2O},\mathrm{MCl_2}) = 2\mathrm{tu}(\mathrm{aq,HCl}) + \mathrm{MCl_2}(\mathrm{aq,HCl}) \tag{2}$$

$$\mathrm{MCl_2}(\mathrm{cr}) + 87\mathrm{HCl}(\mathrm{aq},4640\mathrm{H_2O},2\mathrm{tu}) = \mathrm{MCl_2}(\mathrm{aq,HCl}) + 2\mathrm{tu}(\mathrm{aq,HCl}) \tag{3}$$

$$\mathrm{MCl_2}(\mathrm{cr}) + 2\mathrm{tu}(\mathrm{cr}) = [\mathrm{Mtu_2Cl_2}](\mathrm{cr}) \tag{4}$$

Values of $\Delta H(2)$ and $\Delta H(3)$ were the same as those reported in a previous publication (*1*), there being no detectable effect of the slightly different concentrations used here.

The foregoing reaction scheme was not feasible for the silver complex owing to the insolubility of silver chloride, and for the mercury complex owing to the extremely slow reaction rate. Accordingly a series of reactions 5–8 was devised for [$\mathrm{Agtu_2Cl}$] and another series 9–12 was devised for [$\mathrm{Hgtu_2Cl_2}$], both involving the strongly bonded aqueous thiosulfate complexes of the metal ions.

$$[\mathrm{Agtu_2Cl}](\mathrm{cr}) + 150\mathrm{Na_2S_2O_3}(\mathrm{aq},4000\mathrm{H_2O}) = \mathrm{AgCl}(\mathrm{aq},\mathrm{Na_2S_2O_3}) + 2\mathrm{tu}(\mathrm{aq},\mathrm{Na_2S_2O_3}) \tag{5}$$

$$2\mathrm{tu}(\mathrm{cr}) + 150\mathrm{Na_2S_2O_3}(\mathrm{aq},4000\mathrm{H_2O},\mathrm{AgCl}) = 2\mathrm{tu}(\mathrm{aq},\mathrm{Na_2S_2O_3}) + \mathrm{AgCl}(\mathrm{aq},\mathrm{Na_2S_2O_3}) \tag{6}$$

$$\mathrm{AgCl}(\mathrm{cr}) + 150\mathrm{Na_2S_2O_3}(\mathrm{aq},4000\mathrm{H_2O},2\mathrm{tu}) = \mathrm{AgCl}(\mathrm{aq},\mathrm{Na_2S_2O_3}) + 2\mathrm{tu}(\mathrm{aq},\mathrm{Na_2S_2O_3}) \tag{7}$$

$$\mathrm{AgCl}(\mathrm{cr}) + 2\mathrm{tu}(\mathrm{cr}) = [\mathrm{Agtu_2Cl}](\mathrm{cr}) \tag{8}$$

$$[\mathrm{Hgtu_2Cl_2}](\mathrm{cr}) + 150\mathrm{Na_2S_2O_3}(\mathrm{aq},4000\mathrm{H_2O}) = \mathrm{HgCl_2}(\mathrm{aq},\mathrm{Na_2S_2O_3}) + 2\mathrm{tu}(\mathrm{aq},\mathrm{Na_2S_2O_3}) \tag{9}$$

$$2\mathrm{tu}(\mathrm{cr}) + 150\mathrm{Na_2S_2O_3}(\mathrm{aq},4000\mathrm{H_2O},\mathrm{HgCl_2}) = \mathrm{HgCl_2}(\mathrm{aq},\mathrm{Na_2S_2O_3}) + 2\mathrm{tu}(\mathrm{aq},\mathrm{Na_2S_2O_3}) \tag{10}$$

$$\mathrm{HgCl_2}(\mathrm{cr}) + 150\mathrm{Na_2S_2O_3}(\mathrm{aq},4000\mathrm{H_2O},2\mathrm{tu}) = \mathrm{HgCl_2}(\mathrm{aq},\mathrm{Na_2S_2O_3}) + 2\mathrm{tu}(\mathrm{aq},\mathrm{Na_2S_2O_3}) \tag{11}$$

$$\mathrm{HgCl_2}(\mathrm{cr}) + 2\mathrm{tu}(\mathrm{cr}) = [\mathrm{Hgtu_2Cl_2}](\mathrm{cr}) \tag{12}$$

Table III. Enthalpies of Formation at 298.15 K of Crystalline and Gaseous Thiourea Complexes and Thiourea

complex	$\Delta_f H°(\mathrm{cr})$/kJ mol^{-1}	$\Delta_f H(\mathrm{g})$/kJ mol^{-1}
[$\mathrm{Cotu_2Cl_2}$]	−531.4 ± 3.3	−404.2 ± 7.1
[$\mathrm{Zntu_2Cl_2}$]	−643.6 ± 3.3	−545.7 ± 5.9
[$\mathrm{Cdtu_2Cl_2}$]	−612.9 ± 4.0	−497.8 ± 7.0
[$\mathrm{Agtu_2Cl}$]	−345.8 ± 3.5	−193.9 ± 8.4
[$\mathrm{Hgtu_2Cl_2}$]	−479.3 ± 4.0	−347 ± 26
tu	−92.7[a] ± 2.2	+2.5 ± 5.3

[a] From ref *16*.

Table IV. Mean Coordinate Bond Energies, $\bar{D}$(M–tu) = $\Delta H(13)/2$ at 298.15 K

complex	$\bar{D}$(M–tu)/ kJ mol^{-1}	complex	$\bar{D}$(M–tu)/ kJ mol^{-1}
[$\mathrm{Cotu_2Cl_2}$]	179	[$\mathrm{Agtu_2Cl}$]	148
[$\mathrm{Zntu_2Cl_2}$]	148	[$\mathrm{Hgtu_2Cl_2}$]	104
[$\mathrm{Cdtu_2Cl_2}$]	142		

The enthalpy changes for the formation of the crystalline complexes from crystalline metal chloride and crystalline thiourea, reactions 8 and 12, were calculated respectively from $\Delta H(8) = \Delta H(6) + \Delta H(7) - \Delta H(5)$ and $\Delta H(12) = \Delta H(10) + \Delta H(11) - \Delta H(9)$. Results are in Table II.

An unsuccessful attempt was made to devise a suitable reaction scheme for the copper complex [$\mathrm{Cutu_2Cl}$]. Reaction rates all proved to be too slow for this type of calorimetry.

The complexes, with the exception of [$\mathrm{Hgtu_2Cl_2}$], were thermally stable to temperatures greater than their melting temperatures as shown by the data in Table I. The measured enthalpies of sublimation, $\Delta_{\mathrm{cr}}^{\mathrm{g}}H$, are also reported in this table. The value for thiourea was corrected to 298.15 K by using the heat capacities of the gaseous (*13*) and crystalline (*14*) materials at 298.15 K. The lack of heat capacity data precluded a corresponding calculation for the other compounds. The value for the mercury complex, to which an uncertainty of ±20 % was attached, was estimated by assuming a linear increase in $\Delta_{\mathrm{cr}}^{\mathrm{g}}H$ in the order zinc, cadmium, mercury.

Enthalpies of formation of the crystalline and gaseous complexes, given in Table III, were calculated from the enthalpies of reactions 4, 8, and 12 by using the enthalpies of formation of the metal halides given by Kubaschewski and Alcock (*15*) and the value given by Cox and Pilcher (*16*) for the enthalpy of formation of crystalline thiourea (−92.7 ± 2.2 kJ mol^{-1}). Where these data are also listed by the National Bureau of Standards (*17*) the values are mostly similar, although the enthalpy of formation of thiourea differs by 4.4 kJ mol^{-1}.

Discussion

[$\mathrm{Co^{II}tu_2Cl_2}$] has been shown by infrared (*6*) and X-ray analysis (*18*) to be tetrahedral. X-rays indicate a similar tetrahedral structure for [$\mathrm{Zn^{II}tu_2Cl_2}$] (*19*) and for [$\mathrm{Cd^{II}tu_2Cl_2}$] (*20*). The mercury complex [$\mathrm{Hg^{II}tu_2Cl_2}$] is interesting in that preliminary X-ray studies (*21*), confirmed by later work (*22*), showed that the structure was actually [$\mathrm{Hg^{II}tu_2Cl}$]Cl in which the chlorobis(thiourea) mercury ion was trigonal planar. A quite different arrangement was found (*23*) for [$\mathrm{Ag^{I}tu_2Cl}$] which was shown to consist of infinite spiralling chains of –Ag–S–Ag–S–, each silver atom being surrounded by a distorted tetrahedron of ligands.

The mean metal–sulfur coordinate bond dissociation energy, D(M–tu), may be expressed (*24*) as one half of the value of $\Delta H(13)$

$$\mathrm{Mtu_2Cl}_n(\mathrm{g}) = \mathrm{MCl}_n(\mathrm{g}) + 2\mathrm{tu}(\mathrm{g}) \tag{13}$$

on the assumption that the metal–chlorine bond energy is similar in the complex and in MCl_n. The data from Table III and the enthalpies of sublimation of the metal chlorides (*15*) yield the mean coordinate bond dissociation energies given in Table IV. For the tetrahedral complexes of cobalt, zinc, and cadmium the bond strengths are of the same order as previously found (*2*) for other tetrahedral sulfur-bonded complexes. The highest value, for cobalt, may reflect the additional ligand field stabilization present in this species. Although the silver complex has a distorted structure, the bond energy is close to that of the other tetrahedral complexes. The mercury complex displays considerably weaker bonding. Direct comparison is probably unwise, however, owing to the uncertainty in the value of the enthalpy of sublimation and to the unusual structure of the complex.

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Registry No. tu, 62-56-6; [$Cotu_2Cl_2$], 14240-49-4; [$Zntu_2Cl_2$], 14239-75-9; [$Cdtu_2Cl_2$], 15021-53-1; [$Agtu_2Cl$], 15631-39-7; [$Hgtu_2Cl_2$], 15020-97-0; Co, 7440-48-4; Zn, 7440-66-6; Cd, 7440-43-9; Ag, 7440-22-4; Hg, 7439-97-6.

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Vapor Pressures of Methyl, Ethyl, *n*-Propyl, Isobutyl, and *n*-Butyl Benzoates at Reduced Pressures

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The vapor pressures of methyl, ethyl, *n*-propyl, isobutyl, and *n*-butyl benzoates were measured over the pressure range of 0.50-30 kPa. The results were examined by fitting with a Chebyshev polynomial and with Miller, Frost-Kalkwarf, and Antoine equations. The percent root mean square deviations of pressures of these five benzoates for the Miller fit were 0.30, 0.30, 0.25, 0.16, and 0.24, respectively. The enthalpies of vaporization of the benzoates were also obtained by using a Chebyshev polynomial with mean errors of ±0.2 kJ/mol.

Experimental Section

As few experimental data for alkyl benzoates have been published, the vapor pressure of five benzoates were measured at 0.5-30 kPa.

All the special grade materials from Tokyo Kasei Co., Ltd., were used without further purification. The purities of the materials were determined to exceed 99% by a gas chromatographic analysis with a 3 mm i.d. and 2 m length column packed with 5% silicone (SE52) on celite. Table I shows the densities and refractive indexes compared with the literature values (*1-5*).

The experimental apparatus and procedure were already described elsewhere (*6*). The Multi-Range Model 157/100 pressure standard with a spiral quartz Bourdon tube attached a calibration table from Texas Instruments Inc. was used as a pressure gauge. As the gauge was essentially a difference meter, a McLeod gauge was used in determining zero pressure (less than 0.001 kPa) as a standard pressure. The accuracies of pressures were ±0.002 kPa for the 10-30 kPa range and ±0.001 kPa for 0.50-10 kPa range. Three mercury thermometers with immersion lines marked at the 18-cm points from their bulb ends, i.e., sets of 40-100, 100-150, and 150-200 °C graduations, were used for temperature measurements. They were calibrated in 5-°C intervals with accuracies of ±0.04 K by Watanabe Keiki Seisakusho Co. Ltd., Tokyo. The intermediate temperatures in the intervals were interpolated.

Results and Discussion

The experimental results are presented in Table II. The results are also plotted in Figure 1 including a comparison with values from the literature (*2*, *7-13*).

The Chebyshev polynomial (*14*) and Miller (*15*), Frost-Kalkwarf (*16*), and Antoine equations were used to fit the results.

The Chebyshev polynomial is

$$t \ln P = a_0/2 + \sum a_i E_i(x)$$

where $t = T - 273.15$ K, $E_1(x) = x$, $E_2(x) = 2x^2 - 1$, $E_i(x) = 2xE_{i-1}(x) - E_{i-2}(x)$, and x is a function of temperature defined as

$$x = \frac{2T - (T_{\max} + T_{\min})}{T_{\max} - T_{\min}}$$

where $T_{\max}$ and $T_{\min}$ are the maximum and minimum temperatures of the related substances. The polynomial with four