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A thermochemical study of Cs_2MCl_4 complexes

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Abstract

The standard molar formation enthalpies of Cs_2MCl_4 (M is Zn(II) and Cu(II)) are determined from the enthalpies of dissolution ($\Delta_s H_m^\ominus$) of $[2CsCl(s) + MCl_2(s)]$ and $Cs_2MCl_4(s)$ in 0.03 mol l^{-1} H_2SO_4 solvent, respectively, at 298.2 K, as:

$$\Delta_f H_m^\ominus(Cs_2ZnCl_4,\ s,\ 298.2\,K) = -1340.46\,kJ\,mol^{-1}$$

$$\Delta_f H_m^\ominus(Cs_2CuCl_4,\ s,\ 298.2\,K) = -1129.04\,kJ\,mol^{-1}.$$

Keywords: Cs_2CuCl_4 ; Cs_2ZnCl_4; Standard molar formation enthalpy; Thermochemistry

1. Introduction

A series of tetrahedral tetrahalogen metallic salts, R_2MX_4 (where R is a univalent cation; M(II) is Fe, Co, Ni, Zn, Cu; X is Cl, Br, I), have been prepared and characterized [1,2]. The crystal structures and the magnetic and spectral properties have been previously reported [3–8], but a few thermochemical data have been published. We have determined the standard molar formation enthalpies of Cs_2ZnCl_4 and Cs_2CuCl_4 by solution calorimetry.

Firstly, the dissolution enthalpies ($\Delta_s H_m^\ominus$) of $[2CsCl(s) + MCl_2(s)]$ and $[Cs_2MCl_4(s)]$ in 0.03 mol l^{-1} H_2SO_4 solvent were determined at 298.2 K. Hence, from these values, combined auxiliary values, the standard molar formation enthalpies of $Cs_2ZnCl_4(s)$ and $Cs_2CuCl_4(s)$ have been derived:

$$\Delta_f H_m^\ominus(Cs_2ZnCl_4,\ s,\ 298.2\,K) = -1340.46\,kJ\,mol^{-1};$$
$$\Delta_f H_m^\ominus(Cs_2CuCl_4,\ s,\ 298.2\,K) = -1129.04\,kJ\,mol^{-1}.$$

2. Experimental

2.1. Chemicals

All the chemicals (CsCl, KCl, $ZnCl_2$, $CuCl_2{\cdot}2H_2O$, H_2SO_4) used were of analytical grade and obtained from the Shanghai Reagent Factory.

CsCl with a purity higher than 99.5% was dried in a vacuum oven at 220°C to constant mass, prior to use.

KCl (obtained from Shanghai reagent factory), calorimetric primary standard of purity greater than 99.99%, was dried in a vacuum oven for 6 h at 135°C, prior to use.

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Table 1

Dissolution enthalpies of [2CsCl(s) + $ZnCl_2$(s)], Cs_2ZnCl_4(s), [2CsCl(s) + $CuCl_2 \cdot 2H_2O$(s)], Cs_2CuCl_4(s) in 0.03 mol l^{-1} H_2SO_4 at 298.2 K. (R = 1666.0 Ω, I = 10.000 mA)

System	No.	m [a] (g)	ΔE_s [b] (mV)	ΔE_e [c] (mV)	t_e [d] (s)	Q [e] (J)	$\Delta_s H_m^{\ominus}$ [f] (kJ mol^{-1})
2CsCl(s) + $ZnCl_2$(s)	1	0.4558	0.9364	−1.4168	269.0	−29.73	−30.841
	2	0.4666	0.9498	−1.4042	270.1	−30.44	−30.855
	3	0.4624	0.9442	−1.4096	270.2	−30.15	−30.845
	4	0.4659	0.9516	−1.4064	269.8	−30.39	−30.858
	5	0.4650	0.9493	−1.4077	269.9	−30.32	−30.845
	$\Delta_s H_m^{\ominus}$ [2CsCl(s) + $ZnCl_2$(s)] = −30.849 ± 0.017 kJ mol^{-1}						
Cs_2ZnCl_4(s)	1	0.4558	−0.2606	−1.2386	240.1	8.43	8.747
	2	0.4666	−0.2497	−1.1567	239.8	8.62	8.743
	3	0.4624	−0.2692	−1.2569	239.6	8.55	8.746
	4	0.4659	−0.2562	−1.1880	239.7	8.61	8.744
	5	0.4650	−0.2532	−1.1778	240.4	8.60	8.751
	$\Delta_s H_m^{\ominus}$ [Cs_2ZnCl_4(s)] = 8.746 ± 0.003 kJ mol^{-1}						
[2CsCl(s)+$CuCl_2 \cdot 2H_2O$(s)]	1	0.5124	0.3039	0.7933	268.9	17.162	16.987
	2	0.5132	0.2795	0.7290	269.5	17.214	17.013
	3	0.5132	0.2655	0.6990	269.9	17.079	16.879
	4	0.5098	0.2515	0.6620	268.9	17.020	16.933
	5	0.5080	0.2393	0.6350	270.1	16.951	16.924
	$\Delta_s H_m^{\ominus}$ [2CsCl(s) + $CuCl_2 \cdot 2H_2O$(s)] = 16.947 ± 0.053 kJ mol^{-1}						
Cs_2CuCl_4(s)	1	0.4760	0.1632	0.7039	267.4	10.329	10.224
	2	0.4767	0.1689	0.7300	269.7	10.396	10.275
	3	0.4802	0.1702	0.7280	269.8	10.509	10.311
	4	0.4736	0.1488	0.6562	272.5	10.295	10.242
	5	0.4719	0.1565	0.6800	269.0	10.314	10.298
	$\Delta_s H_m^{\ominus}$ [Cs_2CuCl_4(s)]= 10.270 ± 0.037 kJ mol^{-1}						

[a] Mass of sample.

[b] The voltage change during the sample dissolution.

[c] The voltage change during the electrical calibration.

[d] Heating period of electrical calibration.

[e] Heat effect.

[f] $(= \Delta E_s/\Delta E_e)I^2Rt_e(M/m)$ where R is the electro-resistance; I the current; and M the molar mass.

Table 2

Reaction scheme for the standard molar formation enthalpy of $Cs_2ZnCl_4(s)$ at the temperature 298.2 K. The solvent 's' was 0.03 mol l^{-1} $H_2SO_4(aq)$. $\Delta H_5 = \Delta H_1 - \Delta H_2 + 2\Delta H_3 + \Delta H_4$

Reaction	$\Delta_s H_m^\ominus$ (kJ mol^{-1})
1. $\{2CsCl(s) + ZnCl_2(s)\}$+'s'= $\{2CsCl + ZnCl_2\}$ (sln in 's')	−30.849±0.017
2. $Cs_2ZnCl_4(s)$+'s'= Cs_2ZnCl_4 (sln in 's')	8.746±0.003
3. $Cs(s) + 1/2Cl_2(g) = CsCl(s)$	−443.04
4. $Zn(s) + Cl_2(g) = ZnCl_2(s)$	−415.05
5. $2Cs(s) + Zn(s) + 2Cl_2(g) = Cs_2ZnCl_4(s)$	−1340.46

Table 3

Reaction scheme for the standard molar formation enthalpy of Cs_2CuCl_4 at the temperature 298.2 K. The solvent 's' was 0.03 mol l^{-1} H_2SO_4 (aq). $\Delta H_6 = \Delta H_1 - \Delta H_2 + 2\Delta H_3 + \Delta H_4 - 2\Delta H_5$

Reaction	$\Delta_s H_m^\ominus$ (kJ mol^{-1})
1. $\{2CsCl(s) + CuCl_2 \cdot 2H_2O(s)\}$+'s'= $\{2CsCl + CuCl_2 \cdot 2H_2O\}$ (sln in 's')	16.947±0.053
2. $Cs_2CuCl_4(s)$+'s'= Cs_2CuCl_4 (sln in 's')	10.270±0.0037
3. $Cs(s) + 1/2Cl_2(g) = CsCl(s)$	−443.04
4. $Cu(s) + Cl_2(g) + 2H_2(g) + O_2(g) = CuCl_2 \cdot 2H_2O(s)$	−821.32
5. $H_2(g) + 1/2O_2(g) = H_2O(l)$	−285.84
6. $2Cs(s) + Zn(s) + 2Cl_2(g) = Cs_2ZnCl_4(s)$	−1129.04

2.2. Calorimeter

The isoperibol reaction calorimeter used for this study was constructed in this laboratory and was adapted for measuring enthalpies of solid–liquid, liquid–liquid reactions [9]. The volume of the reaction vessel is 100 cm^3. The precision temperature control and measurement are ±0.001 and ±0.0001 K, respectively.

The calorimeter was tested by measuring the dissolution enthalpy of THAM (NBS 742a, U.S.A.) in 0.1 mol l^{-1} HCl and the KCl (calorimetric primary standard) in water at 298.2 K. The mean dissolution enthalpies are −29776 ± 16 J mol^{-1} for THAM and 17597 ± 17 J mol^{-1} for KCl, which are in conformity with the respective published data [10,11].

2.3. Preparations

$Cs_2ZnCl_4(s)$ was prepared by evaporating a mixture of solutions of CsCl and $ZnCl_2$ (mole ratio is 2 : 1) according to the method of Behler [12].

$Cs_2CuCl_4(s)$ was prepared by evaporating an aqueous solution of cesium chloride and copper chloride (mole ratio is 2 : 1) at ambient temperature and was subsequently purified by means of repeated recrystallization according to Helmholz and Kruh [13].

The structures of the $Cs_2ZnCl_4(s)$ and $Cs_2CuCl_4(s)$ were characterized by state methods [12,13].

3. Results and discussion

All were dissolved in 100 ml of 0.03 mol l^{-1} H_2SO_4 solution.

Sample of mass 0.45 g of CsCl(s) and $ZnCl_2(s)$ in a mole ratio 2 : 1 were dissolved in 100 ml 0.03 mol l^{-1} H_2SO_4 solution at 298.2 K. The results are shown in Table 1.

The dissolution enthalpies of $Cs_2ZnCl_4(s)$, $[2CsCl(s) + CuCl_2 \cdot 2H_2O(s)]$ and $Cs_2CuCl_4(s)$ in 0.03 mol l^{-1} H_2SO_4 were measured under the same conditions. The results are also tabulated in Table 1.

3.1. Cs_2ZnCl_4

The reaction scheme to derive the standard molar formation enthalpy of $Cs_2ZnCl_4(s)$ is given in Table 2. The molar dissolution enthalpy of CsCl(s) and $ZnCl_2(s)$ mixture at mole ratio of $n(CsCl)/n(ZnCl_2) = 2 : 1$ was measured in

0.03 mol l^{-1} H_2SO_4(aq). In the same solvent, we have measured the molar dissolution enthalpy of Cs_2ZnCl_4(s). The standard molar formation enthalpies of CsCl(s) and $ZnCl_2$(s) were taken from Ref. [14]. After combining all the reactions, we obtained: $\Delta_f H_m^\ominus$ (Cs_2ZnCl_4, s, 298.2 K)= −1340.46 kJ mol^{-1}.

3.2. Cs_2CuCl_4

The standard molar formation enthalpy of Cs_2CuCl_4(s) has been derived from the reaction scheme as given in Table 3. The molar dissolution enthalpies of CsCl(s) and $CuCl_2{\cdot}2H_2O$(s) mixture at mole ratio of $n(\mathrm{CsCl})/n(\mathrm{CuCl_2}\cdot 2\mathrm{H_2O}) = 2:1$ was measured in 0.03 mol l^{-1} H_2SO_4(aq). In the same solvent, we have measured the molar dissolution enthalpy of Cs_2CuCl_4(s). The dilution effect of 0.03 mol l^{-1} H_2SO_4 diluted in 2 mol H_2O is ignored. These values were combined with auxiliary quantities of $\Delta_f H_m^\ominus = -443.04$ kJ mol^{-1} for CsCl(s) [14], −821.32 kJ mol^{-1} for $CuCl_2{\cdot}2H_2O$(s) [14] and −285.84 kJ mol^{-1} for H_2O [14] to derive the standard molar formation enthalpy: $\Delta_f H_m^\ominus$ [Cs_2CuCl_4, s, 298.2 K]= −1129.04 kJ mol^{-1}

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