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THERMOCHEMISTRY OF COPPER COMPLEX OF 6-BENZYLAMINO-PURINE

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The copper(II) complex of 6-benzylaminopurine (6-BAP) has been prepared with dihydrated cupric chloride and 6-benzylaminopurine. Infrared spectrum and thermal stabilities of the solid complex have been discussed. The constant-volume combustion energy, $\Delta_c U$, has been determined as –12566.92±6.44 kJ mol^{-1} by a precise rotating-bomb calorimeter at 298.15 K. From the results and other auxiliary quantities, the standard molar enthalpy of combustion, $\Delta_c H_m^\theta$, and the standard molar of formation of the complex, $\Delta_f H_m^\theta$, were calculated as –12558.24±6.44 and –842.50±6.47 kJ mol^{-1}, respectively.

Keywords: *combustion energy, copper(II) complex of 6-benzylaminopurine, rotating-bomb calorimeter, standard enthalpy of formation*

Introduction

Physiologically active compounds are one of the main topics of contemporary chemistry. 6-benzylaminopurine (6-BAP) is a common model compound for one of the most important classes of plant cytokinins [1, 2]. 6-BAP is an active and easily obtainable plant growth promoting substance. It affects a variety of important physiological process and micro-propagation system [3]. In recent several years, 6-BAP and relevant derivatives are received much attention, because purine bases are an integral part of composition of nucleic acids. Particularly, complexes of BAP with transition metals are of considerable interest [4–8]. Recent studies indicate some of the structural features are considered to be effective in cancer chemotherapy [9, 10]. The related research has been devoted to study on anticancer mechanical processes [11], the thermochemical properties of some of these complexes have been studied [12]. However, so far there are no literature data relating to thermochemical properties of cupric complex of 6-BAP. It is necessary to obtain basic thermodynamic data for theoretical researches and practical applications. In the paper, the constant-volume combustion energy of the cupric complex of 6-BAP has been determined by using a rotating-bomb calorimeter. The standard molar enthalpy of combustion and the standard molar enthalpy of the formation of the complex have been calculated, respectively.

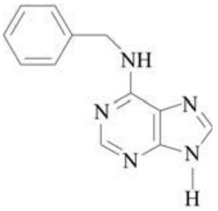

Fig. 1 The structural formula of 6-BAP

Experimental

Materials

Chemicals

6-benzylaminopurine obtained from Changzhou Biological and Chemical Reagent Company was of A. R. grade, with purity ≥99.5%. Chlorhydric acid and cupric chloride dihydrate were of A. R. grade (purchased from Xi'an Chemical Reagent Company). Benzoic acid obtained from Shanghai Reagent Company, calorimetric primary standard of purity >99.999%, was dried in a vacuum oven for 6 h prior to use. All the chemicals proved to be sufficiently reliable to be used without further purification.

Preparation of the complex

The solid complex was prepared by mixing equimolar amounts of 6-BAP and cupric chloride dihydrate in 1.5 mol dm^{-3} solution of chlorhydric acid. The reaction mixture was kept in ultrasonic for 10 min. Yellow-green solution was refluxed for 2 h and left for several days, during which blue needle-shaped crys-

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tals formed. The solid was filtered, washed with 1.5 mol dm^{-3} dilute chlorhydric acid, twice-distilled water, ethanol and diethyl ether, and dried under an infra lamp at 40°C, then kept to be used.

Instrumental methods

Elemental analyzer (Vario EL III CHNIOS, German), IR spectrometer (Bruker EQ UZNDX-550, with KBr pellet, German), melting point instrument (XT-4, Shanghai, China), thermal gravimetric analyzer (Netzsch STA 449C, German), precision rotating-bomb calorimeter (RBC-type II, Northwest University, China), a calorimetric system that is calibrated by benzoic acid with standard calorific value prior to use and the basic experimental procedures used in this investigation have already been described [13, 14]. The initial temperature was 25.0000±0.0005°C, and the initial oxygen pressure was 2.5 kPa. The concrete cross-sectional view of the rotating-bomb is showed as Fig. 1, the bicyclic support as showed in Fig. 2 was used as the holder for the crucible in the oxygen bomb, which facilitates the crucible stable relative to the bomb when the bomb was rotated in crosswise direction and vertically, assuring that the stable final state is attained in a short time. The analytical methods of the final products (solid, liquid and gas) were the same as those in [15], and the analytical results of the final products indicated that the combustion were complete.

Calculation of the energy equivalent of the RBC-type II calorimeter

The energy equivalent of the RBC-type II calorimeter was calculated according to the equation:

$$\Delta_c U = \frac{W\Delta T - aG - 5.97b}{m} \qquad (1)$$

where $\Delta_c U$ (J g^{-1}) is the combustion energy of benzoic acid, *m* (g) is the mass of determined benzoic acid, *W* (J K^{-1}) is the energy equivalent of the RBC-type II calorimeter, *G* (0.9 J cm^{-1}) is the combustion energy of Ni–Cr wire for ignition, *a* (cm) is the length of actual Ni–Cr wire consumed, 5.97 (J mL^{-1}) is the formation enthalpy and solution enthalpy of nitric acid corresponding to 1 mL of 0.1000 mol dm^{-3} solution of NaOH, *b* (mL) is the volume of consumed 0.1000 mol dm^{-3} solution of NaOH and ΔT (K) is the correct value of the temperature rise $\Delta T = \Delta T_{test} + \Delta(\Delta T)$, ($\Delta T_{test} = T_n - T_0$), where $\Delta(\Delta T)$ denotes the correct value of the heat exchange, as obtained from the Eq. (2).

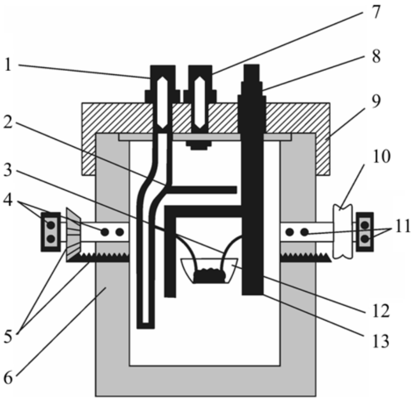

Fig. 2 A cross-sectional view of the rotating bomb; 1 – gas-filled valve, 2 – flame baffle, 3 – Ni–Cr wire for ignition, 4 – ball, 5 – bevel gear, 6 – bomb body, 7 – exhaust valve, 8 – electrode, 9 – bomb cover, 10 – pulley, 11 – ball bearing, 12 – crucible, 13 – crucible support

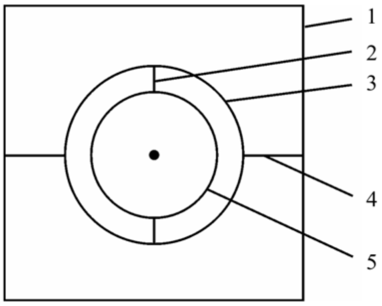

Fig. 3 Bicycle structure of the crucible support in the oxygen bomb; 1 – support, 2 – *x*-axle, 3 – outside ring, 4 – *y*-axle, 5 – inside ring

Correction of the heat exchange

The temperature rise must be corrected on the basis of the heat exchange between the calorimetric tube and its surroundings. The correction of the heat exchange was calculated by means of the following Eq. (2), namely, Linio–Pyfengdelel–Wsava formula, according to the literature [16]:

$$\Delta(\Delta T) = nV_0 + \frac{V_n - V_0}{Q_n - Q_0}\left(\frac{T_0 + T_n}{2} + \sum_{i=1}^{n-1} T_i - nQ_0\right) \quad (2)$$

where $\Delta(\Delta T)$ denotes the correction value of the heat exchange; *n* is the number of readings for the main (or reaction) period; V_0 and V_n are the rate of temperature changes at the initial and the final stages respectively (*V* is positive when temperature decreases); Q_0 and Q_n are the average temperatures of the calorimeter at the initial and the final stages respectively; T_0 is the last reading of the initial stage; T_n is the first reading of the final stage, $\sum_{i=1}^{n-1} T_i$ is the sum of all the temperature readings except for the last one of the main period. $(V_n - V_0)/(Q_n - Q_0)$ is a constant related to the calorimeter performance.

Results and discussion

Characterization of the complex

Elemental analysis, melting point, IR spectrum of the product were studied. The formula $[Cu(C_{12}H_{12}N_5)_2Cl_3]Cl\cdot 2H_2O$ was identified by X-ray diffraction. The results of elemental analysis are in good agreement with those of the X-ray diffraction. The structure determined by means of X-ray diffraction reveals that two water molecules belong to crystal water. The characteristic strong bands of 6-BAP at 1624 and 1598 cm^{-1}, assignable to $\nu_{C=N}$ shift to higher wavenumber at 1655 cm^{-1} in the complex indicating that 6-BAP was coordinated to cupric ion through the nitrogen atom in the complex. The conclusion is in accord with the result confirmed by the X-ray diffraction. Determination of the melting point implies the complex is relatively pure. The results of the complex are summarized in Table 1.

Thermal analysis of the complex

The thermal behavior of $[Cu(C_{12}H_{12}N_5)_2Cl_3]Cl\cdot 2H_2O$ was studied from 25 to 750°C. Thermal gravimetric analysis (TG-DTG) curve of the complex was determined with a Netzsch STA 449C thermal analyzer. The results reveal that the complex decomposes in three steps. The complex eliminates one and half uncoordinated water molecules (found/calcd.: 3.38/3.89%) between 25 to 152°C, a clear mass loss with one overlapped stage is observed from the DTG curve. It is noteworthy that, during this process, the rest crystallization water molecules occurs in the complex. This fact could well be justified because in the crystal structure of the complex the remain water molecules are strongly involved in a complicated hydrogen-bonding network and anchored to the structural building. Then the complex undergoes successive two courses of mass loss up to final steady state (725°C). There are two larger mass loss in above mentioned multi-step decomposition processes. This is probably connected with the skeleton rupture of the corresponding organic ligand. The final product is CuO as revealed by X-ray powder diffraction. The experimental results for final residual amount of mass loss (11.05%) are consistent with the calculated value (11.47%). TG and DTG curves of the investigated complex are presented in Fig. 4.

Calculation of the energy equivalent for the calorimeter

The calorimeter RBC-type II was calibrated by benzoic acid of purity 99.999%. Benzoic acid has an isothermal heat of combustion at 298.15 K of –26434±3 J g^{-1}. The calibrated experimental results with an uncertainty $4.68\cdot 10^{-4}$ are summarized in Table 2.

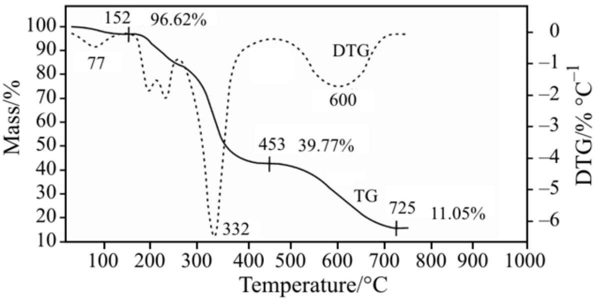

Fig. 4 TG and DTG curves of the complex

Table 1 Color, melting point, elementary analyses and major IR spectra of ligand and the complex*

Compound	Color	*m.p.*/°C	C/%	H/%	N/%	$\nu_{C=N}$/cm^{-1}
Ligand	white	231–232	63.40 (63.18)	4.53 (4.32)	31.62 (31.36)	1624, 1598
Complex	blue	249–250	42.91 (42.60)	3.30 (3.43)	20.85 (20.40)	1655

*The data in brackets are determined values

Table 2 Result for calibration of energy equivalent of the rotating-bomb calorimeter

No.	Mass of complex, *m*/g	Calibrated heat of combustion wire, q_c/J	Calibrated heat of acid, q_N/J	Calibrated Δ*T*/K	Energy equivalent, *W*/J K^{-1}
1	0.99702	10.35	24.78	1.4834	17790.45
2	0.78940	8.10	20.89	1.1746	17789.88
3	0.83060	12.60	20.43	1.2382	17758.93
4	0.96869	12.60	17.43	1.4418	17780.82
5	0.99485	12.60	20.80	1.4800	17798.18
6	1.12328	9.09	21.85	1.6735	17761.41
7	0.90036	9.28	21.67	1.3429	17745.97
Mean					17775.09±7.43

Table 3 The experimental results for the combustion heat of the complex

Sample	No.	Mass of sample, m/g	Calibrated heat of combustion wire, Q_c/J	Calibrated heat of acid, Q_N/J	Calibrated ΔT/K	Combustion energy of sample, $-\Delta_c U$/J g^{-1}
$[Cu(L)_2Cl_3]Cl{\cdot}2H_2O$	1	0.97662	12.60	128.42	1.0039	18127.21
	2	0.95487	12.60	125.77	0.9811	18118.46
	3	0.96850	11.70	128.40	0.9945	18107.62
	4	0.97585	12.60	129.21	1.0011	18089.70
	5	0.98308	12.60	129.74	1.0122	18156.82
	6	0.97533	12.60	128.68	1.0016	18109.00
Mean						18118.14±9.28

L=$C_{12}H_{12}N_5$

Combustion energy of the complex

The determination method of combustion energy for the complex was the same as for the calibration of the calorimeter with benzoic acid. The combustion energy of the complex was calculated according to the formula (3).

$$\Delta_c U = \frac{W\Delta T - aG - Q_N}{m} \tag{3}$$

where $\Delta_c U$ (complex, s) denotes the constant-volume combustion energies of the complex; Q_N is the calibrated heat of acids; m (g) is the mass of the complex; the other symbols are the same as in Eq. (1). The results of experiment are presented in Table 3.

Standard combustion enthalpy of the complex

The standard enthalpy of combustion of the complex, $\Delta_c H_m^\theta$ (complex, s, 298.15 K), refers to the combustion enthalpy change of the following ideal combustion reaction at 298.15 K and 101.325 kPa.

$$[Cu(C_{12}H_{12}N_5)_2Cl_3]Cl{\cdot}2H_2O(s)+59/2O_2(g)= CuO(s)+24CO_2(g)+12H_2O(l)+4HCl(g)+5N_2(g) \tag{4}$$

The standard combustion enthalpy of the complex are calculated by the Eqs (5) and (6).

$$\Delta_c H_m^\theta \text{ (complex, } s\text{, 298.15 K)=} \Delta_c U \text{ (complex, } s\text{, 298.15 K)}+\Delta nRT \tag{5}$$

$$\Delta nRT = n_g \text{ (products)} - n_g \text{ (reactants)} \tag{6}$$

where n_g is the total amount in mole of gases present as products or as reactants, R=8.314 J K^{-1} mol^{-1}, T=298.15 K. The result of the calculation was, namely,

$$\Delta_c H_m^\theta \text{ (complex, } s\text{, 298.15 K)=} -12558.24\pm6.44 \text{ kJ mol}^{-1}$$

Standard formation enthalpy of the complex

The standard enthalpy of formation of the complex, $\Delta_f H_m^\theta$ (complex, s, 298.15 K), was calculated by Hess's law to the following thermochemical Eq. (7).

$$\Delta_f H_m^\theta \text{ (complex, } s\text{)=} \Delta_f H_m^\theta[CuO(s)]+24\Delta_f H_m^\theta[CO_2(g)] +12\Delta_f H_m^\theta[H_2O(l)]+4\Delta_f H_m^\theta[HCl(g)]+ 5\Delta_f H_m^\theta[N_2(g)]-\Delta_c H_m^\theta \text{ (complex, } s\text{)} \tag{7}$$

where

$$\Delta_f H_m^\theta \text{ [CuO(}s\text{), 298.15 K]}=-157.3 \text{ kJ mol}^{-1}$$

$$\Delta_f H_m^\theta \text{ [CO}_2(g)\text{, 298.15 K]}=-393.51\pm0.13 \text{ kJ mol}^{-1}$$

$$\Delta_f H_m^\theta \text{ [H}_2\text{O(}l\text{), 298.15 K]}=-285.83\pm0.04 \text{ kJ mol}^{-1}$$

$$\Delta_f H_m^\theta \text{ [HCl(}g\text{), 298.15 K]}= -92.31\pm0.03 \text{ kJ mol}^{-1} \text{ [17, 18]}$$

The standard molar enthalpy of formation of $[Cu(C_{12}H_{12}N_5)_2Cl_3]Cl{\cdot}2H_2O(s)$, 298.15 K was calculated as –842.50±6.47 kJ mol^{-1}.

Conclusions

The title complex has been synthesized in a given solution of chlorhydric acid. The thermal behavior of the complex was examined by TG-DTG analysis. TG-DTG investigations indicate that the complex is not stable, as the thermal decomposition begins at about 50°C. The combustion energy was determined by an RBC-II rotating-bomb calorimeter. From the combustion energy of the complex and other auxiliary thermodynamic qualities, the standard enthalpy of formation of $[Cu(C_{12}H_{12}N_5)_2Cl_3]Cl{\cdot}2H_2O$ has been calculated to be –842.50±6.47 kJ mol^{-1}.

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