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Preparation and the Standard Enthalpy of Formation on 2-Amino-4, 6-dimethyl-pyrimidine and the Related Complexes of Zinc

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The complexes of zinc chloride and zinc nitrate with 2-amino-4, 6-dimethyl-pyrimidine (ADMP) were prepared through reflux in alcohol. The compositions of the complexes $Zn(ADMP)_2Cl_2$ (**b**) and $Zn(ADMP)_2(NO_3)_2 \cdot 4H_2O$ (**c**) were determined by chemical and elemental analyses. The complexes were characterized by IR, XPS, ^{1}H NMR and TG-DTG techniques. The constant-volume combustion energies of ADMP and the complexes, $\Delta_c E$, were determined by a precise rotating bomb calorimeter at 298. 15K. They were ($-3664. 53 \pm 1. 18$) kJ· mol^{-1}, ($-7130. 94 \pm 3. 69$) kJ· mol^{-1}, and ($-7637. 87 \pm 5. 71$) kJ· mol^{-1}. Their standard enthalpies of combustion, $\Delta_c H_m^{\ominus}$, and standard enthalpies of formation, $\Delta_f H_m^{\ominus}$, were calculated. They were ($-3666. 39 \pm 1. 18$) kJ· mol^{-1}, ($-7129. 70 \pm 3. 69$) kJ· mol^{-1}, ($-7632. 91 \pm 5. 71$) kJ· mol^{-1} and ($19. 09 \pm 1. 43$) kJ· mol^{-1}, ($-411. 96 \pm 4. 03$) kJ· mol^{-1}, ($-1153. 28 \pm 6. 02$) kJ· mol^{-1}.

Keywords: zinc salts   zinc nitrate   2-amino-4, 6-dimethyl-pyrimidine
standard enthalpy of combustion   standard enthalpy of formation

The pyrimidines as a class are known to possess extraordinary biological properties that are generally distinguished qualitatively by their applications in pesticide, herbicide, bactericide, and medicine intermediates[1]. A survey of these applications and a number of the related variations that are developed recently, such as the extraordinary effective herbicide of sulfonyl sulfourea, reveals the broad biological impor-

tance just because of the wide occurrence of pyrimidines ring systems in these molecules[2]. It has been shown that the medicine intermediates in the complexes of metal ions and pyrimidines could prolong the pharmaceutical activity and effective life, and reduce the damage to mammal[1,3~8]. When the complexes of Pt or Pd and pyrimidine are employed as medicine addictives, they are harmful to human body, especially to

some organs such as kidney, although they are identified as the most effective drugs used to treat cancer by now. More positively, the toxicity and the side effect of the complexes of such microelements those are essential to the life as Cu, Zn and Co with pyrimidine would be decreased while the power and efficiency of the medicine are preserved as compared with those of the complexes of Pt and Pd with pyrimidine.

In the present work, the solid complexes of the $ZnCl_2$ and $Zn(NO_3)_2$ with 2-amino-4, 6-dimethyl-pyrimidine (ADMP) were prepared. The compositions of these complexes were determined by chemical and elemental analyses, and the complexes were characterized by IR, XPS, ^1H NMR and TG-DTG techniques. The constant volume – combustion energies of the ADMP and the complexes were determined by a precise rotating bomb, the standard combustion enthalpies and the standard formation enthalpies were calculated. Clearly the study of the complexes is of substantial practical, as well as theoretical, significance.

1 Experimental

1. 1 Reagents and Apparatus

All chemicals and solvents were of anal. grade and used after further purification. Guanidine nitrate and acetylpropyl ketone were made in THE SECOND BRANCH OF THE HEAD REGENT FACTORY OF SHANGHAI; alcohol, $ZnCl_2$, $Zn(NO_3)_2 \cdot 6H_2O$ and K_2CO_3 were purchased from THE CHEMICAL REGENT FACTORY OF XI'AN.

ADMP(**a**) was synthesized according to Ref. [7, 8]. The white solid product with the yield of 99%, and the melting point of 152~152.7℃ when it is 152.9~154.4℃ in the literature[7], was obtained.

Melting point of the compounds was measured with WRS-1A digital melting-point apparatus. Zn^{2+} content was complexometrically determined by EDTA, Cl^- by Fajans' method and C, H, N contents were determined on a Perkin-Elmer 2400 type elemental analyzer. The IR spectra (KBr pellets) were obtained on a Bruker EQ UINOX-550 spectrophotometer in the 400~4000cm^{-1} region. XPS were taken on an ESCA PHI-5400 X-ray

photoelectron spectrophotometer using $MgK\alpha$ radiation, the C_{1s} electron in benzene was used as the internal standard, BE = 284.6eV, and the accuracy of the measured BE value was +0.1eV. The NMR spectra of the compounds were measured with a Varian Unity INOVA- 400 nuclear magnetic resonance spectrometer using TMS as the reference sample and C_2D_5OD as the solvent. TG and DTG data were determined by a Perkin Elmer thermogravimetric analyzer. All TG-DTG tests were performed under a dynamic atmosphere of dry nitrogen at a flow rate of 60mL· min^{-1}, the heating rate used 10℃· min^{-1} and sample masses approximated to 1mg.

The constant-volume combustion energies of the compounds were determined by a precise rotating bomb calorimeter[9]. The main experimental procedures were described in Ref. [10]. The initial temperature was regulated to (25.0000 ± 0.0005)℃, and the initial oxygen pressure was 2.5MPa. The correct value of the heat exchange was calculated according to the Linio-Pyfengdelel-Wsawa formula[11]. The calorimeter was calibrated with benzoic acid of 99.999% purity. It had an isothermal heat of combustion at 298.15K of (−26434 ± 3) J· g^{-1}. The energy equivalent of calorimeter was determined to be (17936.01 ± 9.08) kJ· K^{-1}. The analytical methods for final products (gas, liquid, and solid) were the same as those in Ref. [9].

1. 2 Preparation of the Complexes

For preparation of the complex **b**, 7.39g (0.06 mol) of the ligand and 4.08g (0.03mol) of $ZnCl_2$ were weighed out, and separately dissolved in 40mL and 35mL of alcohol, respectively. When the solution of $ZnCl_2$ was warmed for a few minutes on a hot plate, the solution of the ligand was added dropwise into the solution of salt. Under the condition of reflux, the reaction proceeded further for 3h. After evaporating a part of solvent, the precipitant appeared, and the reaction mixture was allowed to cool slowly to room temperature, followed by suction filtration. In order to remove the reminder of the ligand and salt, it was necessary for the reaction mixture to be rinsed thoroughly with hot alcohol and distilled water. An infrared heat lamp was

employed to serve the drying of the product. Finally, the bottle-green product of the yield of 73% was obtained. According to the procedures used for the complex **b** above, the complex **c** was prepared with the yield of 78%. The purity of the complexes was greater than 99.9% checked by HPLC. The analytical results of the composition of these complexes are presented as follows. For **b**, w_i (calc.): 17.09% Zn, 18.53% Cl, 37.67% C, 4.74% H, 21.96% N; w_i (found): 17.38% Zn, 18.31% Cl, 37.45% C, 4.55% H, 21.75% N. For **c**, w_i (calc.): 12.87% Zn, 28.38% C, 5.16% H, 22.07% N; w_i (found): 12.64% Zn, 28.59% C, 5.34% H, 22.30% N. The compositions of the complexes **b** and **c** were identified as $Zn(ADMP)_2Cl_2$ and $Zn(ADMP)_2(NO_3)_2 \cdot 4H_2O$.

2　Results and Discussion

2.1　IR spectra of the Complexes

　　IR spectra of the ligand and the complexes are shown in Fig. 1. The main characteristic absorption of the title compounds are assigned and listed in Table 1[12, 13]. It is obvious from the infrared spectra of the compounds that there are differences between the main characteristic absorption peaks of the complexes and those of the ligand. Compared with the characteristic absorption peaks of the ligand, the characteristic absorptions of C = N and C-N in the ring of pyrimidine, as well as those of stretching vibration and bending vi-
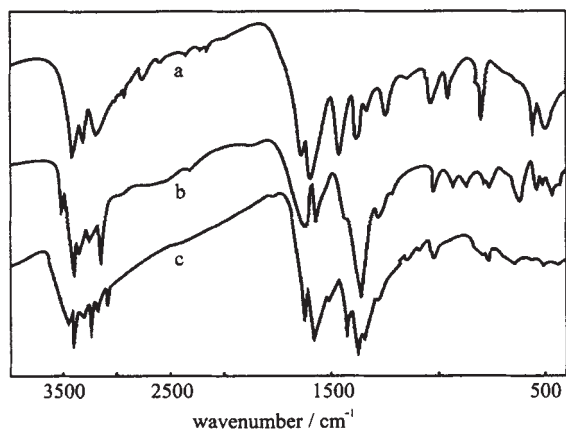

Fig. 1　IR Spectra of the ligand and the complexes
a: ADMP, b: $Zn(ADMP)_2Cl_2$, c: $Zn(ADMP)_2(NO_3)_2 \cdot 4H_2O$

bration of N-H connected with the ring, have the shifts of $28cm^{-1}$, $44cm^{-1}$, $24cm^{-1}$, and $20cm^{-1}$ for the complex **b** and those of $20cm^{-1}$, $47cm^{-1}$, $20cm^{-1}$, and $24cm^{-1}$ for the complex **c**. Based on the analyses above, it is shown that for the ligand the nitrogen atom of the amino group and one of the nitrogen atoms of the pyrimidine coordinate to Zn^{2+} in bidentate fashion. As to the characteristic absorption of NO_3^- for the complex **c**, the peaks of $1433cm^{-1}$, $1349cm^{-1}$, $823cm^{-1}$ were assigned to the vibration absorption peaks of ν_1, ν_2 and ν_3 of NO_3^-, compared with those of ν_1, ν_2 and ν_3 of NO_3^- in $Zn(NO_3)_2$[13], which have little shifts, showing that NO_3^- doesn't participate in coordination to Zn^{2+}. The peaks close to that of $3410cm^{-1}$ and $815cm^{-1}$ in the IR spectra of the complex **c** were regarded as the hydroxyl absorption of water, which was evidence for the presence of water molecule in the complex **c**.

Table 1　Data of IR Absorption for Main Groups of Ligand and Complexes(cm^{-1})

compound	$\nu(C=N)$	$\nu(C\text{-}N)$	$\nu_{as}(N\text{-}H)$	$\nu_s(N\text{-}H)$	$\nu(NO_3^-)$	$\nu(OH^-)$
a	1594	1386	3407	3181		
b	1566	1430	3383	3161		
					1433	
c	1574	1433	3387	3157	1349	3410
					823	815

2.2　XPS Spectra of the Complexes

　　Consulting Ref.[14], the binding energy data obtained from XPS spectra for the internal shell electron of the main atoms of the compounds are listed in Table 2.

　　Three conclusions could be drawn from the analyses of the binding data. 1. Compared with the binding energy of N_{1s} of the amino group and that of N_{1s} of the pyrimidine ring, there are changes for those of the complexes, which shows that nitrogen atom of the amino group and one of the nitrogen atoms in the pyrimidine coordinate to Zn^{2+}. The decrease of the binding energy could be interpreted as that a rather amount of feedback of d electrons existing in the coordination bond of $N \rightarrow Zn^{2+}$ leads to the increase of the electron cloud density of N_{1s}. 2. The binding energies of Cl^- have a distinctly changing, showing that

Table 2　Binding Energy Data(eV)

compound	N_{1s} (amino)	N_{1s} (the ring of pyrimidine)	N_{1s} (nitric acid)	$Cl_{2p_{3/2}}$	$Zn_{2p_{3/2}}$
a	399. 8	398. 5	—	—	—
$ZnCl_2$	—	—	—	199. 1	1023. 1
$Zn(NO_3)_2 \cdot 6H_2O$	—	—	407. 0	—	1022. 9
b	399. 3	399. 1	—	198. 9	1023. 6
c	399. 1	399. 2	407. 2	—	1022. 5

Table 3　Chemical Shifts of the Main Groups for a, b and c

compound	chemical shift δ		
a	2. 304(s, 6H, -CH$_3$)	6. 401(s, 1H, = CH −)	4. 969(s, 2H, -NH$_2$)
b	2. 402(s, 12H, -CH$_3$)	6. 397(s, 2H, = CH −)	4. 900(s, 4H, -NH$_2$)
c	3. 393(s, 12H, -CH$_3$)	6. 438(s, 2H, = CH −)	5. 257(s, 4H, -NH$_2$)

Table 4　Thermoanalytical Results of the Complexes

complex	decomposition product	decomposition temperature*/℃	residual rate**/%
b	$Zn(ADMP)_2Cl_2 \cdot ZnCl_2$	30 ~ 183 ~ 198*	67. 62(67. 82)**
	$ZnCl_2$	198 ~ 240 ~ 328	36. 21(35. 61)
c	$Zn(ADMP)_2(NO_3)_2 \cdot Zn(NO_3)_2$	30 ~ 178 ~ 251	49. 53(49. 43)
	$Zn(NO_3)_2$	251 ~ 324 ~ 360	37. 47(37. 30)
	ZnO	360 ~ 543 ~ 700	16. 21(15. 95)

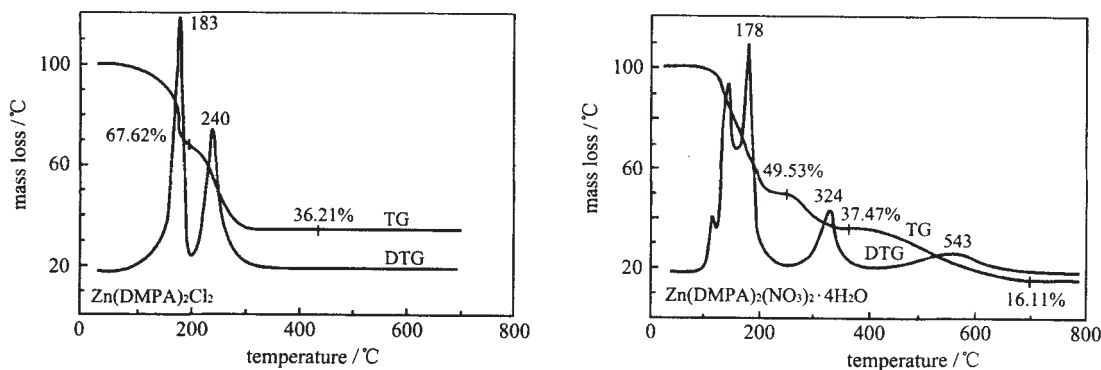*The intermediate data were peak temperatures of DTG curves, **The data in brackets were calculated values.

Fig. 2　TG-DTG curves of the title complexes

Cl$^-$ coordinates to Zn^{2+} while NO$_3^-$ does not. 3. For the complexes **b** and **c**, the binding energy of Zn^{2+} has changes of 0. 5eV and 0. 4eV respectively and the ranges of the differences are not wide, which illustrates a certain degree of feedback bond existing in the coordination bond. It is consistent with the analyses results of infrared spectrum.

2. 3　^{1}H NMR Spectra of the Ligand and the Complexes

The chemical shifts for the main group of ^{1}H NMR spectra of the ligand and the complexes are illustrated in Table 3, showing that two ligands coordinate to Zn^{2+} for the complexes **b** and **c**.

2. 4　Thermostability of the Complexes

Thermostability of the solid complexes was investigated by TG-DTG and the TG curves of the complexes are depicted in Fig. 2. The curves of TG-DTG concerning the compounds reflect that the experimental results for the residual amount of loss of weight are in good agreement with the calculated results, and the intermediate and final products of the thermal decomposition of the complexes are identified by IR spectra as well. The thermal decomposition processes of the complexes are summarized in Table 4.

Obviously, the complex **b** is decomposed into zinc

chloride after processing skeleton splitting of part of the ligand. As for the complex **c**, the first step in the decomposition of the complex losses four molecular of water accompanying skeleton splitting of part of the ligand, followed by loss of reminder of the ligand, and in the last step the complex is decomposed into zinc oxide.

2. 5　Combustion Energies, Standard Enthalpies of Combustion and Standard Enthalpies of Formation of the Ligand and the Complexes
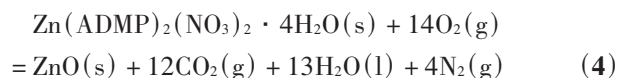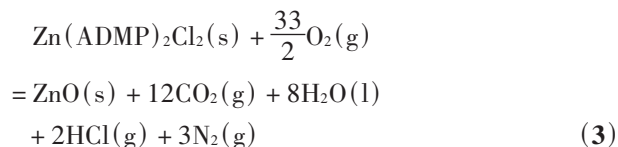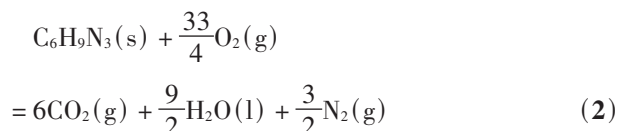
Standard enthalpies of formation of ligand and complexes are studied. The determination method of constant volume combustion energy for the sample is the same as the calibration of the calorimeter with benzoic acid. The combustion energies of the samples are calculated by the formula

$$\Delta_c E(\text{samples, s}) = \frac{W\Delta T - aG - 5.983\text{J} \cdot \text{cm}^{-3} \cdot b}{m} \quad (1)$$

where $\Delta_c E(\text{sample, s})$ denotes the constant volume combustion energy of the samples, W is the energy equivalent of the RBC-Ⅱ type calorimeter (in J· K^{-1}), ΔT the correct value of the temperature rising, **a** the length of actual Ni-Cr wire consumed (in cm), G the

combustion enthalpy of Ni-Cr wire for ignition (0.9J· cm^{-1}), 5.983 the formation enthalpy and solution enthalpy of nitric acid corresponding to $1cm^3$ of 0.1000mol· dm^{-3} solution NaOH (in J· cm^{-3}), **b** the volume in cm^3 of consumed 0.1000mol· dm^{-3} solution of NaOH and **m** the mass in g of the sample. The results of the calculations are given in Table 5.

The standard combustion enthalpies of the compounds, $\Delta_c H_m$, are referred to the combustion enthalpy change of the following ideal combustion reaction at 298.15K and 101.325kPa.

$$C_6H_9N_3(s) + \frac{33}{4}O_2(g)$$
$$= 6CO_2(g) + \frac{9}{2}H_2O(l) + \frac{3}{2}N_2(g) \quad (2)$$
$$Zn(\text{ADMP})_2Cl_2(s) + \frac{33}{2}O_2(g)$$
$$= ZnO(s) + 12CO_2(g) + 8H_2O(l)$$
$$+ 2HCl(g) + 3N_2(g) \quad (3)$$
$$Zn(\text{ADMP})_2(NO_3)_2 \cdot 4H_2O(s) + 14O_2(g)$$
$$= ZnO(s) + 12CO_2(g) + 13H_2O(l) + 4N_2(g) \quad (4)$$

The standard combustion enthalpies of the samples are calculated by the following equations

$$\Delta H_{m,c} = \Delta E_c + \Delta nRT \quad (5)$$

Table 5　Constant-Volume Combustion Energies of a, b and c

compound	No	mass of sample /(m· g^{-1})	calibrated heat of combustion wire q_c/J	calibrated heat of acid containing nitrogen q_n/J	calibrated ΔT/K	combustion energy of sample $-\Delta_c E$/(J· g^{-1})
a	1	0.80525	12.60	70.91	1.3344	29725.72
	2	0.69770	12.60	61.44	1.1567	29736.82
	3	0.74586	12.60	65.68	1.2378	29768.32
	4	0.78249	9.00	68.91	1.2986	29773.94
	5	0.80021	12.60	70.47	1.3266	29738.03
	6	0.79233	12.60	69.77	1.3155	29782.50
	mean					29754.22 ± 9.60
b	1	1.10586	12.60	280.23	1.1589	18599.27
	2	1.11432	11.70	282.28	1.1693	18625.04
	3	1.10476	12.60	279.85	1.1602	18639.82
	4	1.06375	11.70	269.48	1.1186	18663.70
	5	1.20030	10.80	304.01	1.2603	18638.24
	6	1.18525	12.60	300.21	1.2460	18659.42
	mean					18637.58 ± 9.64
c	1	1.03579	12.60	66.00	0.8675	15000.16
	2	1.10246	12.60	70.25	0.9246	15021.50
	3	1.15315	12.60	73.48	0.9701	15068.65
	4	1.14230	11.70	72.78	0.9600	15054.02
	5	1.12312	12.60	71.56	0.9449	15069.37
	6	1.11585	12.60	71.10	0.9368	15037.30
	mean					15041.83 ± 11.2

Table 6   Combustion Energies, Standard Enthalpies of Combustion and Standard Enthalpies of Formation of a, b and c(kJ· mol^{-1})

compound	$-\Delta_{c, compound(s)} E$	$-\Delta_{c\ compound\ s} H_m^{\ominus}$	$-\Delta_{f\ compound\ s} H_m^{\ominus}$
a	3664. 53 ± 1. 18	3666. 39 ± 1. 18	− 19. 09 ± 1. 43
b	7130. 94 ± 3. 69	7129. 70 ± 3. 69	411. 96 ± 4. 03
c	7637. 87 ± 5. 71	7632. 91 ± 5. 71	1153. 28 ± 6. 02

$$\Delta n = n_g(\text{products}) - n_g(\text{reactants}) \qquad (6)$$

where n_g is the total amount of substance (in mole) of gases present as products or reactants, $k = 8.314$J· mol^{-1}· K^{-1}, $T = 298.15$K. The results of the calculations are given in Table 6.

The standard enthalpies of formation of the samples, $-\Delta_c H_m^{\ominus}$, are calculated by Hess's law according to the following thermochemical equations

$$\Delta_{f\ DMP\ s} H_m^{\ominus} = 6\Delta_{f\ CO_2\ g} H_m^{\ominus} + \frac{9}{2}\Delta_{f\ H_2O\ l} H_m^{\ominus}$$
$$- \Delta_{c\ DMP\ s} H_m^{\ominus} \qquad (7)$$

$$\Delta_{f\ Zn\ ADMP\ _2Cl_2\ s} H_m^{\ominus} = [\Delta_{f\ ZnO\ s} H_m^{\ominus} + 12\Delta_{f\ CO_2\ g} H_m^{\ominus}$$
$$+ 8\Delta_{f\ H_2O\ l} H_m^{\ominus} + 2\Delta_{f\ HCl\ g} H_m^{\ominus}]$$
$$- \Delta_{c\ Zn\ ADMP\ _2Cl_2\ s} H_m^{\ominus} \qquad (8)$$

$$\Delta_{f\ Zn\ ADMP\ _2\ NO_3\ _2\cdot\ 4H_2O\ s} H_m^{\ominus} = [\Delta_{f\ ZnO\ s} H_m^{\ominus} + 12\Delta_{f\ CO_2\ g} H_m^{\ominus}$$
$$+ 9\Delta_{f\ H_2O\ l} H_m^{\ominus}]$$
$$- \Delta_{c\ Zn\ ADMP\ _2\ NO_3\ _2\cdot\ 4H_2O\ s} H_m^{\ominus} \quad (9)$$

where $\Delta_{f\ ZnO\ s} H_m^{\ominus} = (-350.46 \pm 0.27)$ kJ · mol^{-1}, $\Delta_{f\ CO_2\ g} H_m^{\ominus} = (-393.51 \pm 0.13)$kJ· mol^{-1}, $\Delta_{f\ H_2O\ l} H_m^{\ominus} = (-285.83 \pm 0.042)$ kJ · mol^{-1}, $\Delta_{f\ HCl\ g} H_m^{\ominus} = (-92.31 \pm 0.03)$ kJ· mol$^{-1[15]}$. The detailed list of the results of the calculations is presented in Table 6.

As described in Table 6, if thermo stabilizations of the complexes are compared with that of the ligand, their values decrease in the order of Zn (ADMP)$_2$(NO$_3$)$_2$· 4H$_2$O, Zn(ADMP)$_2$Cl$_2$ and ADMP, which is related to the structures of the substances.

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