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Preparation, crystal structure and thermochemistry of Zn(AMP)₂Cl₂

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Abstract

The complex of zinc chloride and 2-amino-4,6-dimethyloxyl pyrimidine (AMP) was prepared, and the composition of the complex was determined by chemical and elemental analyses. Complex was characterized by IR, XPS, ¹H NMR and TG–DTG techniques. In addition X-ray structural analysis was performed. Crystals of [Zn(AMP)₂Cl₂] revealed the following parameters: $M_r = 446.59$; orthorhombic *Pbca*; a = 13.0208 (10); b = 13.8531 (11); c = 20.0652 (15) Å; V = 3619.3 (5) Å³; Z = 8; $D_{calc} = 1.639$ Mg m⁻³; Mo K $\alpha \lambda = 0.71073$ Å; $\mu = 1.683$ mm⁻¹; T = 293 K; R = 0.0431 for 2510 observed reflections. The constant-volume combustion energies of the ligand and the complex, $\Delta_c E$, were determined by a precise rotating-bomb calorimeter at 298.15 K. They were -3340.01 ± 1.54 and -6552.76 ± 3.55 kJ mol⁻¹, respectively. Their standard enthalpy of combustion, $\Delta_c H_m^{\theta}$, and standard enthalpy of formation, $\Delta_f H_m^{\theta}$, were calculated, which were -3339.39 ± 1.54 , -6546.56 ± 3.35 and -307.91 ± 1.74 , -995.10 ± 3.93 kJ mol⁻¹. © 2003 Elsevier B.V. All rights reserved.

Keywords: Zinc chloride; 2-Amino-4,6-dimethyloxyl pyrimidine; Standard enthalpy of combustion; Standard enthalpy of formation; Zn(AMP)₂Cl₂

1. Introduction

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 were developed recently, such as the extraordinary effective herbicide of sulfonyl sulfourea, reveals the broad biological importance 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 organ such as kidneys, although they are identified as the most effective drugs used to treat cancer by now. If Pt and Pd in these complexes were replaced by such microelements that are necessary for the life as Cu, Zn or Co, etc., the toxicity and the side effect of these complexes would be decreased while the power and efficiency of the medicine are preserved.

In this work, on the base of the literature [7,8], the synthesis of 2-amino-4,6-dimethyloxyl pyrimidine (AMP) was ameliorated using triethylbenzylamine chloride (TEBA) as catalyst and the yield was improved. The solid complex of ZnCl₂ and AMP were prepared in alcohol, the compositions of the complex were determined by chemical and elemental analyses, and the complex was characterized by spectral measurements (IR, XPS, NMR). In addition X-ray structural analysis was performed. The constant-volume combustion energies of the ligand and the complex were determined by a precise rotating-bomb calorimeter, the standard combustion enthalpy and the standard formation enthalpy were calculated. Clearly the study of the complex is of substantial practical, as well as theoretical significance for further application.

2. Experimental

2.1. Materials

All chemicals and solvents are of analytical grade and used after further purification. Guanidine nitrate and

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diethyl malonate were made in the chemical factory of Shanghai; phosphorus oxychloride, alcohol, ZnCl₂, triethylbenzylamine chloride, and sodium methylate were made in the chemical factory of Xi'an.

2.2. Ligand preparation

2-Amino-4,6-dihydroxyl pyrimidine was synthesized according to [9]. The white solid product of the yield of 80%, with the melting point of exceeding $330 \,^{\circ}$ C, was obtained.

Referred to [9], the synthesis method of 2-amino-4,6-dichloride pyrimidine was ameliorated by selecting TEBA as catalyst and constant agitating vigorously. The straw yellow product with the yield of 80% was obtained, mp = 224-225 °C which was better than that of the literature, 223-225 °C.

Finally, combining the results above and the literature [9], the white crystal of AMP was collected. The yield of AMP was beyond 80%, and its melting point is in the range of 97.0–97.5 °C. Analytically calculated for C₆H₉N₃O₂: C, 46.43; H, 5.85; N, 27.09. Found: C, 46.35; H, 5.98; N, 27.20. ¹H NMR spectrum shows the following peaks: δ (–OCH₃) 3.757, δ (=CH⁻) 5.347, δ (–NH₂) 6.563.

2.3. Preparation of complex

The 1.95 g of the ligand and 0.86 g of ZnCl₂ were separately dissolved in 30 and 10 cm³ of alcohol. When the solution of ZnCl₂ 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 is 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 white product of the yield of 78.5% with the melting point of 193.5-194.6°C was obtained. Crystals suitable for X-ray analysis were obtained by recrystallization of power sample from alcohol solution. The analytical results of the composition of the complex are presented as follows. Analytically calculated for C₆H₉Cl₂N₃O₂Zn: C, 32.91; H, 4.18; Cl, 15.94; N, 19.20; Zn, 13.98. Found: C, 32.41; H, 4.08; Cl, 15.95; N, 18.90; Zn, 14.29. ¹H NMR spectrum shows the following peaks: δ (-CH₃) 3.795, δ (=CH⁻) 5.343, δ (-NH₂) 6.559.

2.4. Instrumentation

Melting point of the compounds was measured with WRS-1A digital melting-point apparatus. C, H, N contents were determined on a Perkin-Elmer 2400 type elemental analyzer. Zn^{2+} was determined complexometrically with EDTA. Infrared spectra were recorded on a Bruker EQ

UINOX-550 spectrophotometer, samples were in KBr discs for 4000–400 cm⁻¹. XPS were taken on a ESCA PHI-5400 X-ray photoelectron spectrophotometer using Mg K α radiation, the C_{1s} electron in benzene was used as the internal standard, BE = 284.6 eV, and the accuracy of the measured BE value was +0.1 eV. The NMR spectra were carried out with a Varian Unity INOVA-400 nuclear magnetic resonance spectrometer using TMS as the reference sample and C₂D₅OD as the solvent. All TG–DTG tests were performed with a Perkin-Elmer thermogravimetric instrument. The purge gas was oxygen flow of 60 ml min⁻¹. A heating rate of 10 °C min⁻¹ was adopted, with samples weighing about 1 mg.

2.5. X-ray data collection of the complex

Data collected for $0.339 \text{ mm} \times 0.303 \text{ mm} \times 0.295 \text{ mm}$ colorless crystal on a Bruker SMART APEX CCD-based diffractometer with graphite-monochromated Mo K α ($\lambda =$ 0.71073 Å) radiation with $2\theta - \omega$ scans. A complex of $M_r =$ 446.59 crystallized in the orthorhombic space group *Pbca*; a = 13.0208 (10); b = 13.8531 (11); c = 20.0652 (15) Å; V = 3619.3 (5) Å³; Z = 8; $D_{calc} = 1.639 \text{ Mg m}^{-3}$; Mo K α $\lambda = 0.71073$ Å; $\mu = 1.683 \text{ mm}^{-1}$; T = 293 K; 4350 reflections were collected for the 2θ range 4.06–56.52°, and 2510 independent reflections with $I > 2\sigma(I)$ were used in the refinement, $R_{int} = 0.0726$. The structures were solved with the direct methods of SHELXS-97 and refined with full- matrix least-squares technique using SHELXL-97. Non-hydrogen atoms were refined anistropically. The hydrogen atoms of the organic ligands were generated geometrically.

2.6. Determination of constant-volume combustion energy

The constant-volume combustion energies of the compounds were determined by a precise rotating-bomb calorimeter [10]. The main experimental procedures were described in [11,12]. The initial temperature was regulated to 25.0000 \pm 0.0005 °C, and the initial oxygen pressure was 2.5 MPa. The correct value of the heat exchange was calculated according to Linio–Pyfengdelel–Wsawa formula [13]. The calorimeter was calibrated with benzoic acid of 99.999% purity. It had an isothermal heat of combustion at 298.15 K of $-26434 \pm 3 \text{ J g}^{-1}$. The energy equivalent of calorimeter was determined to be 17936.01 \pm 9.08 kJ K⁻¹. The analytical methods of final products (gas, liquid and solid) were the same as those in [13].

3. Results and discussion

3.1. Crystal structure

The complex crystallizes in the orthorhombic space group Pbca. Coordination sphere of a Zn(II) forms a distorted tetrahedron geometry with two chlorines and two nitrogen atoms



Fig. 1. The ORTEP drawing of the [Zn(AMP)₂Cl₂] molecule.

in pyrimidine (Fig. 1). Unlike the reported similar complex [14], which exist equivalent Zn–Cl or Zn–N distances, in this complex, Zn–Cl (1), Zn–Cl (2), Zn–N (1) and Zn–N (4) distances are 2.2657 (7), 2.2782 (7), 2.0526 (17) and 2.0684 (17) Å, respectively. The Cl–Zn–Cl angle is 109.46 (3)°, N (1)–Zn–N (4) is 118.25 (8)°, while N (1)–Zn–Cl (1), N (4)–Zn–Cl (1), N (1)–Zn–Cl (2) and N (4)–Zn–Cl (2) angle are 109.02 (5), 106.01 (5), 105.23 (5) and 108.71 (5)°, respectively.

Due to the coordination of two chlorines, the N (3)-H (9) and N (6)-H (17) group form an intermolecular interaction with Cl (1) and Cl (2), respectively, the N(3) \cdots Cl(1) and $N(6) \cdots Cl(2)$ distances being 3.181 and 3.220 Å, while the N (3)-H (8) and N (6)-H (18) group form an weak intermolecular interaction with Cl (2)[x + 1/2, y, -z + 3/2] and Cl(1)[x - 1/2, -y + 1/2, -z + 1], respectively, the $N(3) \cdots Cl(2)$ and $N(6) \cdots Cl(1)$ distances being 3.526 and 3.534 Å. The H · · · Cl distance is shorter than the sum of the entity radii (ca. 3.0 Å) and, therefore, could be considered as a hydrogen bonding interaction, moreover, intermolecular H-bond are stronger than intermolecular H-bond, which can be seen from the $H \cdots Cl$ distance, $H(9) \cdots Cl(1)$ 2.403, $H(17) \cdots Cl(2) 2.436, H(8) \cdots Cl(2)[x+1/2, y, -z+3/2]$ 2.712, H(18) \cdots Cl(1)[x - 1/2, -y + 1/2, -z + 1] 2.733 Å. For H 8, H 9, H 17, and H 18, the calculated angles N-H...Cl are 169.22, 160.16, 153.97, and 165.29°, respectively.

3.2. IR spectrum of the complex

The characteristic absorptions of C=N and C–N in the ring of pyrimidine have the shifts of 27 and 14 cm^{-1} in contrast with those of the free ligand, indicating that nitrogen atom in the pyrimidine binds with zinc ion.

3.3. XPS spectrum of the complex

Consulting [15], the binding energy data of the internal shell electron for the main atoms of the compounds obtained from XPS spectra of the complex are listed in Table 1.

Comparing with the binding energy of N_{1s} in the pyrimidine ring, there is a marked change for that of the complex, which shows that one of the nitrogen atoms in the pyrimidine coordinates to Zn^{2+} . The decrease of the binding energy could be interpreted that rather amount of feedback of

Table 1 Binding energy data (eV)

Compound	N_{1s} (the ring of pyrimidine)	$Cl_{2p_{3/2}}$	$Zn_{2p_{3/2}}$
AMP	398.2	_	_
ZnCl ₂	-	199.4	1023.1
Zn(AMP) ₂ Cl ₂	399.8	198.2	1023.2

d electrons existing in the coordination bond of $N \rightarrow Zn^{2+}$ leads to the increase of the electron cloud density of N_{1s}. The binding energy of Cl⁻ for the complex changes distinctly, which is assumed that Cl⁻ coordinates to Zn²⁺. The binding energy of Zn²⁺ had a little change, illustrating certain degree of feedback bond existing in the coordination bond.

3.4. Thermostability of the complex

The TG–DTG curves of the complex are shown in Fig. 2. The appearance of peaks in the TG-DTG curves suggest that the thermal decomposing process of the complex Zn(AMP)₂Cl₂ occurs in three steps. The first stage begins at 60 °C and completes at 217 °C, accompanying with 65.47% mass loss. It is in agreement with the calculated value of the mass loss of 65.26%, corresponding to the skeleton splitting of the complex. At the second stage of 217-285 °C, the skeleton of the complex is further spitted, the mechanism of this process is same as that of the first stage. In the last step during the range of 401–796 °C, the complex is completely transformed into the final product. This process proceeds with 30.18% mass loss, which coincides with the calculated value of the mass loss 30.50%, preliminarily showing the final product is ZnCl₂. In order to understand the decomposition processes of the complex, decomposition-interruption tests were conducted with TG-DTG experiments and the infrared analyses of the compounds before and after thermal decomposition are performed. The experimental results show that, the IR spectrum of the final product is identical with that of the standard spectra ZnCl₂, while IR spectra of the products at the ends of the first and second stages combine the IR spectrum of the complex Zn(AMP)₂Cl₂ with that of ZnCl₂.



Fig. 2. The TG-DTG curves of the complex.

Complex	Decomposition product	Decomposition temperature (°C)	Residual rate (%)
Zn(AMP) ₂ Cl ₂	$Zn(AMP)_2Cl_2 \cdot ZnCl_2$	60–93–217 ^a	65.47 (65.26) ^b
	$Zn(AMP)_2Cl_2 \cdot 2ZnCl_2$	217-244-285	52.96 (53.68)
	ZnCl ₂	401–514–796	30.18 (30.50)

Table 2Thermo analytical result of the complex

^a The intermediate data are peak temperatures of DTG curves.

^b The data in brackets are calculated values.

In accordance with the IR spectra and TG–DTG experiments described above, it is assumed that the thermal decomposition processes for the complex are summarized in Table 2.

3.5. Standard enthalpy of formation of the complex

Standard enthalpies of formation of the ligand and the complex 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 energy of the sample is calculated by the formula:

$$\Delta_{\rm c} E({\rm s}) = \frac{W\Delta T - aG - 5.983b}{m} \tag{1}$$

where $\Delta_c E(s)$ denotes the constant-volume combustion energy of the sample, *W* is the energy equivalent of the RBC- Π type calorimeter (J K⁻¹), ΔT the correct value of the temperature rising, *a* the length of actual Ni–Cr wire consumed (cm), *G* the combustion enthalpy of Ni–Cr wire for ignition (0.9 J cm⁻¹), 5.983 the formation enthalpy and solution enthalpy of nitric acid corresponding to 1 cm⁻³ of 0.1000 mol dm⁻³ solution NaOH (J cm⁻³), *b* the volume (cm⁻³) of consumed 0.1000 mol dm⁻³ solution of NaOH

Table 3 Experimental results for combustion energies of ligand and complex

and m the mass (g) of the sample. The results of the calculations are given in Table 3.

The standard combustion enthalpy of the compound, $\Delta_c H_m$, refers to the combustion enthalpy change of the following ideal combustion reaction at 298.15 K and 101.325 kPa.

$$C_{6}H_{9}N_{3}O_{2_{(g)}} + \frac{29}{4}O_{2_{(g)}} = 6CO_{2_{(g)}} + \frac{9}{2}H_{2}O_{(l)} + \frac{3}{2}N_{2_{(g)}}$$
⁽²⁾

$$Zn(AMP)_{2}Cl_{2(s)} + \frac{29}{2}O_{2(g)}$$

=ZnO_(s) + 12CO_{2(g)}+8H₂O_(l) + 2HCl_(g) + 3N_{2(g)} (3)

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

$$\Delta_{\rm c} H_m = \Delta_{\rm c} E + \Delta n R T \tag{4}$$

$$\Delta n = n_{\rm g}({\rm products}) - n_{\rm g}({\rm reactants}) \tag{5}$$

where n_g is the total amount in mole of gases present as products or reactants, $k = 8.314 \text{ J} \text{ mol}^{-1} \text{ K}^{-1}$, T = 298.15 K. The results of the calculations were given in Table 3.

Standard enthalpies of formation of the samples, $\Delta_c H_m^{\theta}$, are calculated by Hess's law according to the following thermochemical equations:

Compound	No.	Mass of sample (<i>m</i> (g))	Calibrated heat of combustion wire $(q_c (J))$	Calibrated heat of acid containing nitrogen $(q_n (J))$	Calibrated ΔT (K)	Combustion energy of sample $(-\Delta_c E (J g^{-1}))$
AMP	1	0.77961	12.60	67.17	0.9369	21530.39
	2	1.03304	12.60	89.38	1.2400	21509.09
	3	1.90079	12.60	78.28	1.0912	21560.98
	4	1.00319	12.60	86.60	1.2038	21501.25
	5	1.01272	12.60	87.42	1.2179	21509.37
	6	1.00303	12.60	86.58	1.2040	21509.15
	Mean					21526.70 ± 9.95
Zn(AMP)2Cl2	1	0.97340	11.70	221.92	0.8063	14670.59
	2	0.96461	12.60	221.10	0.7980	14649.46
	3	0.98419	12.60	224.98	0.7995	14679.33
	4	0.96372	12.60	220.30	0.7899	14691.99
	5	0.95479	12.60	218.26	0.7994	14650.09
	6	0.96352	12.60	220.25		14693.22
	Mean					14672.45 ± 7.94

Table 4

Combustion energies, standard enthalpies of combustion and standard enthalpies of formation of the ligand and the complex (kJ mol⁻¹)

Compound	$-\Delta_{c,compound(s)}E$	$-\Delta_{c,compound(s)}H_m^{\theta}$	$-\Delta_{\mathrm{f,compound}(\mathrm{s})}H_m^{\theta}$
AMP	$\begin{array}{r} 3340.01 \pm 1.54 \\ 6552.76 \pm 3.55 \end{array}$	3339.39 ± 1.54	307.91 ± 1.74
Zn(AMP) ₂ Cl ₂		6546.56 ± 3.55	995.10 ± 3.93

$$\Delta_{\mathrm{f},\mathrm{AMP}(\mathrm{s})}H_{m}^{\theta} = \left[6\Delta_{\mathrm{f},\mathrm{CO}_{2}_{(\mathrm{g})}}H_{m}^{\theta} + \frac{1}{2}\Delta_{\mathrm{f},\mathrm{H}_{2}\mathrm{O}_{(\mathrm{l})}}H_{m}^{\theta}\right] -\Delta_{\mathrm{c},\mathrm{AMP}(\mathrm{s})}H_{m}^{\theta}$$
(6)

$$\Delta_{\mathrm{f,Zn}(\mathrm{AMP})_{2}\mathrm{Cl}_{2_{(\mathrm{s})}}}H_{m}^{\theta} = \left[\Delta_{\mathrm{f,ZnO}_{(\mathrm{s})}}H_{m}^{\theta} + 12\Delta_{\mathrm{f,CO}_{2_{(\mathrm{g})}}}H_{m}^{\theta} + 8\Delta_{\mathrm{f,H}_{2}\mathrm{O}_{(\mathrm{l})}}H_{m}^{\theta} + 2\Delta_{\mathrm{f,HCl}_{(\mathrm{g})}}H_{m}^{\theta}\right] - \Delta_{\mathrm{c,Zn}(\mathrm{AMP})_{2}\mathrm{Cl}_{2_{(\mathrm{s})}}}H_{m}^{\theta}$$
(7)

where $\Delta_{f,ZnO_{(s)}} H_m^{\theta} = -348.28 \pm 0.27 \text{ kJ mol}^{-1}$, $\Delta_{f,CO_{2(g)}} H_m^{\theta} = -393.51 \pm 0.13 \text{ kJ mol}^{-1}$, $\Delta_{f,H_2O_{(l)}} H_m^{\theta} = -285.83 \pm 0.042 \text{ kJ mol}^{-1}$ [16]. The detailed list of the results of the calculations is presented in Table 4.

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References

- P.Z. Zhang, J. Wu, Y.Q. Gong, Chin. J. Appl. Chem. 17 (2000) 558.
 C.L. Liu, Pesticides 34 (1995) 25.
- [3] P.Z. Zhang, Y.Q. Gong, X.Q. Shi, Chem. Res. Appl. 9 (1997) 92.
- [4] L.K. Mishra, J. Indian Chem. Soc. 59 (1982) 408.
- [5] R. Melanson, F.D. Rochon, Can. J. Chem. 57 (1979) 526.
- [6] J.R. Allan, J. Therm. Anal. 22 (1981) 3.
- [7] E.B. Singh, O.P. Cupta, J. Indian Chem. Soc. 64 (1987) 359.
- [8] P. Lumme, H. Elo, Inorg. Chim. Acta 92 (1984) 241.
- [9] K.Q. Xu, Handbook of Fine Industrial Chemicals and Intermediate, Beijing Chemical and Industrial Press, Beijing, 1998.
- [10] J.R. Liu, X.W. Yang, Y.D. Hou, Thermochim. Acta 329 (1999) 123.
- [11] X.F. Yang, X.W. Yang, L.Z. Sun, Chem. J. Chin. Univ. 7 (1986) 363.
- [12] X.W. Yang, X.F. Yang, Q.Z. Zhang, T.C. Zhang, L. Jin, J. Northwest Univ. (Nat. Sci. Ed.) 26 (1996) 122.
- [13] M.M. Popov, Thermometry and Calorimetry, Moscow University, Publishing House, Moscow, 1954, p. 382.
- [14] E. Szlyk, A. Wojtczal, M. Jaskólski, M. Gilski, J.G. Haasnoot, J. Reedijk, Inorg. Chim. Acta 260 (1997) 145.
- [15] K. Nakamoto, Infrared and Roman Spectra of Inorganic and Coordination Compounds, Beijing Chemical and Industrial Press, Beijing, 1991.
- [16] J.D. Cox, J. Chem. Thermodyn. 10 (1978) 903.