# Standard Enthalpies of Formation for Solid Complexes of Chromium Chloride with L- $\alpha$ -Amino Acids

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The solid complexes of  $Cr(AA)_2Cl_3\cdot nH_2O$  of  $CrCl_3$  with  $L\text{-}\alpha$ -amino acids (AA = Val, Leu, Thr, Met, Arg, Phe, Try and His) have been prepared in 95% EtOH medium, and characterized structurally by elemental analysis, chemical analysis, IR spectra and TG-DTG. The constant-volume combustion energies of the complexes have been determined by RBC-II type rotating-bomb calorimeter. The standard enthalpies of formation of the complexes have been calculated as well, which are (-2543.16  $\pm$  3.71) (Val), (-2561.32  $\pm$  4.06) (Leu), (-2284.02  $\pm$  2.95) (Thr), (-1418.77  $\pm$  4.60) (Met), (-3218.91  $\pm$  4.67) (Arg), (-2643.90  $\pm$  5.02) (Phe), (-1707.18  $\pm$  3.23) (Try) and (-2838.05  $\pm$  3.45) (His) kJ/mol, respectively.

**Keywords** chromium chloride, *L-α*-amino acids, solid complex, characterization, standard enthalpy of formation

### Introduction

GTF, the indispensable cofactor of insulin, is a complex formed between amino acid, niacin and chromium. Insulin does not keep the normal sugar metabolic unless GTF has affinity for its complex. Thus, it is desirable to have a good understanding of coordination behavior of chromium with amino acid in order to get acquaintance with GTF. <sup>2</sup>

Considering the complexes of chromium with valine, lucien, methionine and phenylanine, much effort has been made for their preparations and properties on spectrum, and magnetism in mixed solvent of water and alcohol. <sup>3-8</sup> The structure, biological activity, chromatography

and spectrum for these complexes (the molar ratio of chromium to amino acid is 1:2) and the relationship between the complexes with GTF have been studied by Cooper. 1 Gao and co-workers9 investigated the solubility property of Cr(NO<sub>3</sub>)<sub>3</sub>-His-H<sub>2</sub>O, disclosed the existence of the new solid complexes of Cr(His)(NO<sub>3</sub>)<sub>3</sub>·3H<sub>2</sub>O, Cr- $(His)_2(NO_3)_3 \cdot 3H_2O$  and  $Cr(His)_3(NO_3)_3 \cdot 3H_2O$ , determined the enthalpies of the reaction of Cr(NO<sub>3</sub>)<sub>3</sub> with histidine, and calculated the thermokinetic parameters and thermodynamic parameters. In our present work, eight solid complexes of Cr(AA)2Cl3 · nH2O of CrCl3 with  $L-\alpha$ -amino acids (AA = Val, Leu, Thr, Met, Arg, Phe, Try and His) have been prepared in 95% EtOH medium and characterized by chemical analysis, elemental analysis, IR spectra and TG-DTG. The constant volume combustion energies of these complexes have been determined by a RBC-II type rotating-bomb calorimeter, and the standard enthalpies of formation of these complexes have been calculated as well.

### **Experimental**

Preparation of the complexes

CrCl<sub>3</sub>•6H<sub>2</sub>O (A.R.) and L- $\alpha$ -amino acids were recrystallized as the purity of 99.95%. CrCl<sub>3</sub>•6H<sub>2</sub>O and L- $\alpha$ -amino acids with the molar ratio of 1:2 were blended in 95% EtOH. After refluxing at 70—80 °C with a water bath for 6 h, the solution was evaporated to remove a

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large amount of alcohol from the mixture, and then filtered. The precipitate was obtained and dried with  $P_2O_5$  in a desiccator. The analytical results on the composition of the complexes are summarized in Table 1. The purity of the complexes is excellent than 99.99%. The sample was checked by HPLC: LC-6A type, PC 8-10 s<sup>-1</sup> 2504 column, and mobile phase: solution (1) 10% of methanol in water, solution (2) 90% of methanol in water.

## Apparatus and experimental procedure

The constant-volume combustion energies of the complexes were determined with a RBC-II type rotating-bomb calorimeter. <sup>10</sup> Based on a RBC-I type rotating-bomb, <sup>11</sup> a RBC-II type rotating-bomb with digital indicator wherein integrated circuit employed, aiming at promoting the precision and accuracy of the experimental thermochemistry, was developed. The accuracy of the present calorimeter was improved from  $1.6 \times 10^{-3}$  to  $4.68 \times 10^{-4}$  by calibration with the standard benzoic acid with purity of 99.999%. Benzoic acid has an isothermal heat of combustion of -26434 J/g at 25 °C. The calibrated ex-

perimental results are presented in Table 2. The calibration for the apparatus and temperature, and the determination processes of the experiment in addition to the analyses of final products are identical with Ref. 11.

The IR spectra of the compounds were obtained with a Bruker EQ UINOX-550 model infrared spectrophotometer (KBr paller). TG and DTG data were collected with a Perkin Elmer thermogravimetric analyzer. All TG-DTG tests were performed under a dynamic atmosphere of dry oxygen at a flow rate of 60 mL/min and the heating rate of 10 deg./min, and approximately 1 mg of the sample masses were used.

The IR absorption of main groups for the complexes and ligands are depicted in Table 3, which is interpreted as follows: 12,13

- (1) The characteristic absorption peaks of amino and carboxyl groups in the complexes have shifted greatly as compared to those in the pure ligand. It indicated that nitrogen and oxygen atoms in the complexes coordinated to Cr<sup>3+</sup> in a bidentate fashion.
- (2) The characteristic absorption peaks of hydroxyl, methylthio, benzol, indolyl and imidazolyl group in the complexes shifted a little bit as compared with corre-

Table 1	Analytical	reaults of	composition	of	complexes	(%)	) a
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Complex	Cr <sup>3+</sup>	CI-	С	Н	N
A [Cr(Val) <sub>2</sub> Cl <sub>3</sub> ·H <sub>2</sub> O]	12.73 (12.66)	26.07 (25.90)	29.31 (29.25)	5.94 (5.89)	6.79 (6.82)
$\mathbf{B} \left[ \mathbf{Cr} (\mathbf{Leu})_2 \mathbf{Cl}_3 \cdot \mathbf{H}_2 \mathbf{O} \right]$	11.67 (11.85)	24.65 (24.24)	32.94 (32.85)	6.49 (6.43)	6.33 (6.39)
$\mathbf{C} \left[ \mathbf{Cr} (\mathbf{Thr})_2 \mathbf{Cl}_3 \cdot 4\mathbf{H}_2 \mathbf{O} \right]$	11.14 (11.09)	22.71 (22.69)	20.61 (20.50)	5.64 (5.59)	5.91 (5.98)
$\mathbf{D} \left[ \mathbf{Cr}(\mathbf{Met})_2 \mathbf{Cl}_3 \cdot 2\mathbf{H}_2 \mathbf{O} \right]$	10.67 (10.55)	21.60 (21.58)	24.42 (24.37)	5.37 (5.32)	5.64 (5.68)
$\mathbf{E}\left[\operatorname{Cr}(\operatorname{Arg})_{2}\operatorname{Cl}_{3}\cdot\operatorname{H}_{2}\operatorname{O}\right]$	9.88 (9.91)	20.30 (20.27)	27.56 (27.47)	5.81 (5.67)	21.30 (21.35)
$\mathbf{F}\left[\operatorname{Cr}(\operatorname{Phe})_{2}\operatorname{Cl}_{3}\cdot\operatorname{H}_{2}\operatorname{O}\right]$	10.35 (10.26)	21.01 (20.99)	42.73 (42.66)	4.84 (4.77)	5.51 (5.53)
$\mathbf{G}\left[\operatorname{Cr}(\operatorname{Try})_{2}\operatorname{Cl}_{3}\cdot\operatorname{H}_{2}\operatorname{O}\right]$	7.36 (7.31)	14.87 (14.96)	37.21 (37.17)	5.71 (5.67)	7.86 (7.88)
$\mathbf{H} \left[ \mathbf{Cr}(\mathbf{His})_2 \mathbf{Cl}_3 \cdot \mathbf{H}_2 \mathbf{O} \right]$	10.77 (10.69)	21.89 (21.85)	29.68 (29.62)	4.19 (4.14)	17.26 (17.27)

<sup>&</sup>lt;sup>a</sup> Cr<sup>3+</sup> was determined with ammonium ferrous sulfate. Cl<sup>-</sup> was determined by Fajan method. Carbon, hydrogen and nitrogen analyses were performed on a 2400 type elemental analyzer (PE Company, USA). The data in brackets are calculated values.

Table 2 Calibrated experimental results for the energy equivalent of the calorimeter using benzoic acid

No.	Mass of benzoic acid A (g)	Calibrated heat of combustion wire $q_{\rm c}$ (J)	Calibrated heat of acid containing nitrogen $q_N$ (J)	Calibrated temperature $\Delta T$ (K)	Energy equivalent of calorimeter W (J/K)
1	0.76823	10.80	23.96	1.1281	18032.22
2	0.80052	12.60	25.22	1.1783	17990.98
3	0.86965	12.60	22.70	1.2808	17975.97
4	0.81237	11.70	23.06	1.1959	17985.58
5	0.80250	12.60	24.28	1.1802	18005.56
6	0.79825	12.60	24.03	1.1734	18013.95
Mean					18000.71 ± 8.42

Table 3 Data of IR absorption for main groups of ligands and complexes (cm<sup>-1</sup>)

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Compd	$\nu_{\mathrm{NH_3}^+}^{\mathrm{as}}$	ν <sup>8</sup> NH <sub>3</sub> +	$\delta_{\mathrm{NH_3}^+}^{\mathrm{as}}$	$\delta_{\mathrm{NH_3}^+}^*$	As	R							
Compu	$\nu_{\mathrm{NH}_2}^{\mathrm{88}}$	$\nu_{\mathrm{NH_2}}^{8}$	$\delta_{ m NH_2}^{ m as}$	$\delta^{\rm s}_{ m NH_2}$	ν <sup>as</sup> COO -	ν <sup>8</sup> coo <sup>-</sup>	νOH	NOH	<sup>у</sup> СОН	ν <sub>SCH<sub>3</sub></sub>	ν <sub>C</sub> 6H <sup>2</sup>	ν accin	ν <sup>8</sup> CCN
Val	3455	2977	1615	1506	1600	1426							
Leu	3454	2958	1613	1514	1583	1407	_		_	_			
Thr	3441	2959	1627	1456	1564	1417	_		1107	_	_		_
Met	3124	2100	1620	1510	1582	1410		_		1340		_	
Arg	3301	3097	1683	<b>156</b> 1	1614	1420		_		_	_		
Phe	3028	2130	1629	1496	1567	1413				_	1074	_	
Try	3404	3038	1667	1456	1 <b>5</b> 91	1357	_		_		_	1315	743
His	3025	2860	1590	1456	1635	1415	_	_	1315			_	_
A	3419	3106	1624	1447	1500	1447	3409	824			_		_
В	3418	2694	1626	1452	1501	1355	3410	825			_	_	
C	3403	3051	1624	1449	1495	1346	3400	825	_				
D	3100	2365	1656	1499	1626	1448	3410	825	_	1351			_
E	3399	3182	1 <b>66</b> 1	1447	1506	1350	3409	824	-	_	_		_
F	3032	2367	1626	1446	1498	1347	3410	824			1084	_	
G	3406	2977	1736	1500	1629	1450	3409	825		_	_	1353	750
<u>H</u>	3135	3023	1627	1443	1504	1384	3423	828			_	1155	978

sponding to the ligands of Thr, Met, Phe, Try and His. This confirmed that the hydroxyl, methylthio, benzol, indolyl and imidazolyl groups did not participate in coordination to chromium.

(3) The characteristic absorptions of 3390—3423 cm<sup>-1</sup> and 823—828 cm<sup>-1</sup> in the complexes are assigned to those of water. The existence of water molecule for the complexes is believable as indicated by the elemental analysis.

# Thermostability of the complexes

Thermostability of the solid complexes investigated by TG-DTG and the TG curves of the complexes are depicted in Fig. 1. The curves of TG reflects that the experimental results for the residual amount of loss of weight are in best agreement with the calculated results. IR spectra of intermediate products are identical with those of the corresponding solid complexes except that the characteristic absorption of water is not visible, and IR spectra of final products (CrCl<sub>3</sub> or Cr<sub>2</sub>O<sub>3</sub>) of the thermal decomposition of the complexes are consisted with those of Santlar standard spectra. The thermal decomposition processes of the complexes are summarized in Table 4.

Obviously, the complexes of A—F were decomposed into chromium hemitrioxide, while the complexes of G and H were decomposed into chromium chloride after pro-

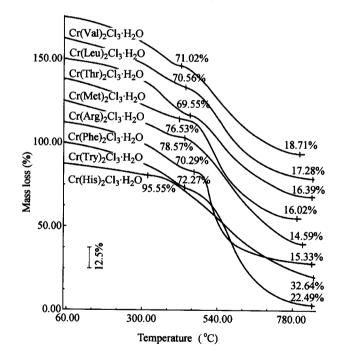


Fig. 1 TG curves for the complexes in an atmosphere of oxygen. cessing water loss and skeleton splitting of part of amino acid.

Constant-volume combustion energies and standard enthalpies

The constant-volume combustion energies of the

complexes determined by a RBC-II type rotating-bomb

calorimeter are summarized in Table 5.

Table 4 Thermoanalytical results of the complexes

Complex	Decomposition product	Decomposition temperature (℃)	Residual rate (%)
A	4Cr(Val) <sub>2</sub> Cl <sub>3</sub> ·3CrCl <sub>3</sub>	51—345—420°	71.02 (71.16) <sup>b</sup>
	$Cr_2O_3$	420553800	18.71 (18.51)
В	$4Cr(Leu)_2Cl_3\cdot 3CrCl_3$	51—33 <del>6</del> —439	70.56 (70.27)
	$Cr_2O_3$	439—526—840	17.28 (17.32)
C	4Cr(Thr) <sub>2</sub> Cl <sub>3</sub> ·3CrCl <sub>3</sub>	51—368—458	69.55 (69.42)
	$Cr_2O_3$	458—535—841	16.39 (16.22)
D	9Cr(Met) <sub>2</sub> Cl <sub>3</sub> ·4CrCl <sub>3</sub>	51308421	76.53 (76.59)
	$Cr_2O_3$	421530800	16.02 (16.07)
E	8Cr(Arg) <sub>2</sub> Cl <sub>3</sub> ·3CrCl <sub>3</sub>	51—340—421	78.57 (78.46)
	$Cr_2O_3$	421 <del>656</del> 815	14.59 (14.48)
F	3Cr(Phe) <sub>2</sub> Cl <sub>3</sub> ·2CrCl <sub>3</sub>	51—350—466	70.29 (70.87)
	$Cr_2O_3$	466—516—838	15.33 (15.00)
G	2Cr(Try) <sub>2</sub> Cl <sub>3</sub> ·CrCl <sub>3</sub>	51—248—435	72.27 (72.40)
	CrCl₃	435—515—841	22.49 (22.27)
H	7Cr(His) <sub>2</sub> Cl <sub>3</sub> ·CrCl <sub>3</sub>	51—17 <del>6</del> —301	91.55 (91.57)
	CrCl₃	301—542—745	32.46 (32.54)

<sup>&</sup>lt;sup>a</sup> Intermediate data are peak temperatures of DTG curves. <sup>b</sup> Data in brackets are calculated values.

Table 5 Experimental results for combustion energies of the complexes

Complex	No.	Mass of sample A(g)	Calibrated heat of combustion wire $q_{ m c}$ (J)	Calibrated heat of acid containing nitrogen $q_{ m N}$ (J)	Calibrated temperature $\Delta T$ (K)	Combustion energy of sample $-\Delta_{c,\cos}E (J \cdot g^{-1})$
	1	0.90376	11.70	128.36	0.6452	12697.11
	2	0.91823	12.60	130.43	0.6577	12737.59
	3	0.89913	12.60	127.81	0.6434	12724.80
A	4	0.91002	12.60	129.35	0.6505	12711.27
	5	0.99436	10.80	141.34	0.7127	12748.87
	6	0.95396	12.60	135.60	0.6808	12960.98
	mean					$12718.44 \pm 9.30$
	1	1.01290	12.60	100.21	0.8526	15040.57
	2	1.06365	11.70	105.23	0.8947	15031.55
	3	1.05271	11.70	104.15	0.8875	15065.67
В	4	1.10034	12.60	108.86	0.9242	15008.81
	5	1.02580	12.60	101.49	0.8637	15044.96
	6	1.10489	9.90	109.31	0.9295	15035.39
	mean					$15037.83 \pm 7.57$
	1	1.00235	12.60	142.45	0.6037	10686.86
	2	1.10357	12.60	156.83	0.6649	10691.88
	3	0.98732	11.70	140.31	0.5936	10668.49
C	4	0.99095	10.80	140.83	0.5953	10660.67
	5	0.99724	12.60	141.72	0.6009	10691.82
	6	0.97369	12.60	138.37	0.5853	10665.45
	mean					$10677.53 \pm 5.82$

Complex	No.	Mass of sample	Calibrated heat of combustion wire	Calibrated heat of acid containing nitrogen	Calibrated temperature	Continue Combustion energy of sample
		A (g)	q <sub>c</sub> (J)	$q_{\mathrm{N}}$ (J)	ΔT (K)	$-\Delta_{c,\cos}E \left(\mathbf{J} \cdot \mathbf{g}^{-1}\right)$
	1	0.92200	3.60	1019.44	0.8097	14698.63
	2	0.91852	12.60	1015.29	0.8055	14671.04
	3	0.89047	12.60	984.57	0.7876	14720.53
D	4	0.93578	12.60	1034.67	0.8216	14685.20
	5	0.95696	11. <b>70</b>	1058.09	0.8425	14729.78
	6	0.90233	11.70	997.69	0.7913	14703.02
	mean					$104701.37 \pm 8.88$
	1	0.94532	7.20	247.65	0.6360	11841.07
	2	0.90379	9.90	236.77	0.6077	11830.58
	3	0.93240	11.70	244.36	0.6284	11857.24
E	4	0.89798	12.60	235.24	0.6036	11823.64
	5	0.91095	12.60	238.64	0.6121	11819.52
	6	093478	12.60	244.88	0.6308	11871.64
	mean					$11840.62 \pm 8.31$
	1	1.12140	9.90	189.00	1.0302	16359.40
	2	1.02358	12.60	172.51	0.9422	16388.71
	3	1.09462	12.60	184.48	1.0046	16340.31
F	4	1.00355	11.70	169.13	0.9230	16375.69
	5	1.05727	12.60	178.18	0.9702	16337.84
	6	1.10033	12.60	185.44	1.0095	16334.81
	mean					$16356.13 \pm 9.12$
	1 2	0.57580	9.00	118.82	0.5578	17216.01
	2	0.57370	9090	118.56	0.5568	17246.53
	3	0.60434	11.70	124.71	0.5862	17234.68
G	4	0.61236	12.60	126.36	0.5949	17260.54
	5	0.59305	12.60	122.38	0.5744	17207.03
	6	0.59487	11.70	122.76	0.5772	17239.99
	mean					$17234.13 \pm 8.06$
	1	0.88680	12.60	196.92	0.5351	10625.45
	2	0.89721	12.60	190.23	05401	10599.92
	3	0.90547	11.70	201.07	0.5468	10635.38
H	4	0.90634	12.60	201.26	0.5476	10639.86
	5	0.88756	12.60	197.09	0.5351	10616.17
	6	0.91036	12.60	202.15	0.5485	10609.69
	mean					$10621.08 \pm 6.27$

The standard combustion enthalpy of the complexes,  $\Delta_{\rm c,\,coor}\,H_{\rm m}^{\theta}$ , refers to the combustion enthalpy change of the following ideal combustion reaction at 298.15 K and

101.325 kPa.

The standard combustion enthalpies of the complexes were calculated from the combustion energy by the Eqs. (1)—(8).

$$Cr(Leu)_2Cl_3 \cdot H_2O(s) + \frac{33}{2}O_2(g) = \frac{1}{2}Cr_2O_3(s) + 12CO_2(g) + 3HCl(g) + \frac{25}{2}H_2O(l) + N_2(g)$$
 (2)

$$Cr(Thr)_{2}Cl_{3} \cdot 4H_{2}O(s) + \frac{19}{2}O_{2}(g) = \frac{1}{2}Cr_{2}O_{3}(s) + 8CO_{2}(g) + 3HCl(g) + \frac{23}{2}H_{2}O(l) + N_{2}(g)$$
(3)

$$Cr(Met)_{2}Cl_{3} \cdot 2H_{2}O\ (s) + \frac{31}{2}O_{2}\ (g) = \frac{1}{2}Cr_{2}O_{3}\ (s) + 10CO_{2}\ (g) + 3HCl\ (g) + \frac{23}{2}H_{2}O\ (l) + 2SO_{2}(g) + N_{2}\ (g)(4)$$

$$Cr(Arg)_2Cl_3 \cdot H_2O(s) + 17O_2(g) = \frac{1}{2}Cr_2O_3(s) + 12CO_2(g) + 3HCl(g) + \frac{27}{2}H_2O(l) + 4N_2(g)$$
 (5)

$$Cr(Phe)_{2}Cl_{3} \cdot 4H_{2}O(s) + \frac{43}{2}O_{2}(g) = \frac{1}{2}Cr_{2}O_{3}(s) + 18CO_{2}(g) + 3HCl(g) + \frac{21}{2}H_{2}O(l) + N_{2}(g)$$
 (6)

$$Cr(Try)_{2}Cl_{3} \cdot 8H_{2}O(s) + 26O_{2}(g) = \frac{1}{2}Cr_{2}O_{3}(s) + 22CO_{2}(g) + 3HCl(g) + \frac{37}{2}H_{2}O(l) + 2N_{2}(g)$$
(7)

$$\Delta_{c, coor} H_m^{\theta} = \Delta_{c, coor} E + \Delta nRT$$
 (9)

products or as reactants,  $R = 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ , T = 298.15 K.

$$\Delta n = n_{\rm g}({\rm products}) - n_{\rm g}({\rm reactants})$$
 (10)

The standard formation enthalpies of the complexes, were calculated by Hess's law according to the thermochemical Eqs. (11)—(18).

where  $n_{\rm g}$  is the total amount (in moles) of gas present as

$$\Delta_{f,A(s)} H_{m}^{\theta} = \left[ \frac{1}{2} \Delta_{f,Cr_{2}O_{3}(s)} H_{m}^{\theta} + 10 \Delta_{f,CO_{2}(g)} H_{m}^{\theta} + 3 \Delta_{f,HCl(g)} H_{m}^{\theta} + \frac{21}{2} \Delta_{f,H_{2}O(1)} H_{m}^{\theta} \right] - \Delta_{c,A(s)} H_{m}^{\theta}$$
(11)

$$\Delta_{f,B(s)} H_{m}^{\theta} = \left[ \frac{1}{2} \Delta_{f,C_{z_{2}O_{3}(s)}} H_{m}^{\theta} + 12 \Delta_{f,CO_{2}(g)} H_{m}^{\theta} + 3 \Delta_{f,HCl(g)} H_{m}^{\theta} + \frac{25}{2} \Delta_{f,H_{z}O(1)} H_{m}^{\theta} \right] - \Delta_{c,B(s)} H_{m}^{\theta}$$
(12)

$$\Delta_{f,C(s)} H_{m}^{\theta} = \left[ \frac{1}{2} \Delta_{f,C_{r_{2}O_{3}(s)}} H_{m}^{\theta} + 8\Delta_{f,CO_{2}(g)} H_{m}^{\theta} + 3\Delta_{f,HCl(g)} H_{m}^{\theta} + \frac{33}{2} \Delta_{f,H_{2}O(l)} H_{m}^{\theta} \right] - \Delta_{c,C(s)} H_{m}^{\theta}$$
(13)

$$\Delta_{\rm f,D(s)} H_{\rm m}^{\theta} = \left[ \frac{1}{2} \Delta_{\rm f,Cr_2O_3(s)} H_{\rm m}^{\theta} + 10 \Delta_{\rm f,CO_2(g)} H_{\rm m}^{\theta} + 3 \Delta_{\rm f,HCl(g)} H_{\rm m}^{\theta} + \frac{23}{2} \Delta_{\rm f,H_2O(l)} H_{\rm m}^{\theta} + 2 \Delta_{\rm f,SO_2(g)} H_{\rm m}^{\theta} \right] - \Delta_{\rm c,D(s)} H_{\rm m}^{\theta}$$
 (14)

$$\Delta_{f,E(s)} H_{m}^{\theta} = \left[ \frac{1}{2} \Delta_{f,C_{2}O_{3}(s)} H_{m}^{\theta} + 12\Delta_{f,CO_{2}(g)} H_{m}^{\theta} + 3\Delta_{f,HCl(g)} H_{m}^{\theta} + \frac{27}{2} \Delta_{f,H_{2}O(1)} H_{m}^{\theta} \right] - \Delta_{c,E(s)} H_{m}^{\theta}$$
(15)

$$\Delta_{f,F(s)} H_{m}^{\theta} = \left[ \frac{1}{2} \Delta_{f,C_{z_{0}}O_{3}(s)} H_{m}^{\theta} + 18\Delta_{f,CO_{z}(g)} H_{m}^{\theta} + 3\Delta_{f,HCl(g)} H_{m}^{\theta} + \frac{21}{2} \Delta_{f,H_{z}O(1)} H_{m}^{\theta} \right] - \Delta_{c,F(s)} H_{m}^{\theta}$$
(16)

$$\Delta_{f,C(s)} H_{m}^{\theta} = \left[ \frac{1}{2} \Delta_{f,C_{z_{2}O_{3}(s)}} H_{m}^{\theta} + 22 \Delta_{f,CO_{2}(g)} H_{m}^{\theta} + 3 \Delta_{f,HCl(g)} H_{m}^{\theta} + \frac{37}{2} \Delta_{f,H_{2}O(1)} H_{m}^{\theta} \right] - \Delta_{c,G(s)} H_{m}^{\theta}$$
(17)

$$\Delta_{f,H(s)}H_{m}^{\theta} = \left[\frac{1}{2}\Delta_{f,C_{z_{2}O_{3}(s)}}H_{m}^{\theta} + 12\Delta_{f,CO_{2}(g)}H_{m}^{\theta} + 3\Delta_{f,HCl(g)}H_{m}^{\theta} + \frac{17}{2}\Delta_{f,H_{2}O(1)}H_{m}^{\theta}\right] - \Delta_{c,H(s)}H_{m}^{\theta}$$
(18)

Table 6 Combustion energies, standard enthalpies of combustion and standard enthalpies of formation of the complexes

Complex	$-\Delta_{c,\cos}E$ (J/g)	$-\Delta_{c,coor}H_m^{\theta}$ (kJ/mol)	$-\Delta_{\rm f, coor} H_{\rm m}^{\theta}$ (kJ/mol)
A	$6597.38 \pm 3.32$	6598.62 ± 3.32	2543.16 ± 3.71
В	$5223.02 \pm 3.82$	$5221.78 \pm 3.82$	$2561.32 \pm 4.06$
C	$5004.09 \pm 2.72$	$4997.89 \pm 2.72$	$2284.02 \pm 2.95$
D	$7245.02 \pm 4.38$	$7243.78 \pm 4.38$	$1418.77 \pm 4.60$
E	$6213.66 \pm 4.36$	$6208.71 \pm 4.36$	$3218.91 \pm 4.67$
${f F}$	$8288.52 \pm 4.62$	$8287.28 \pm 4.62$	$2643.90 \pm 5.20$
${f G}$	$7876.58 \pm 2.76$	$7872.24 \pm 2.76$	$1707.18 \pm 3.23$
H	$5169.09 \pm 3.05$	$5160.41 \pm 3.05$	$2838.05 \pm 3.45$

where  $\Delta_{\rm f,\,Cr_2O_3(s)}H_{\rm m}^\theta=-1139.70~{\rm kJ/mol}\,,~~\Delta_{\rm f,\,CO_2(g)}H_{\rm m}^\theta=(-393.51\pm0.13)~{\rm kJ/mol}\,,~~\Delta_{\rm f,\,HCl(g)}H_{\rm m}^\theta=(-92.31\pm0.03)~{\rm kJ/mol}\,,~~\Delta_{\rm f,\,SO_2(g)}H_{\rm m}^\theta=(-296.81\pm0.02)~{\rm kJ/mol}\,,~~\Delta_{\rm f,\,H_2O(1)}H_{\rm m}^\theta=(-285.83\pm0.042)~{\rm kJ/mol}\,.^{14}$  Combustion energies, standard enthalpies of combustion and standard enthalpies of formation of the complexes are presented in Table 6. Obviously, the standard formation enthalpies of the complexes vary with the structures of amino acids .

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