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# THERMOCHEMISTRY OF THE COMPLEXES OF CHROMIUM NITRATE WITH *L*-α-AMINO ACIDS

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## Abstract

The solid complexes of $Cr(NO_3)_3$ with *L*-α-amino acids (*AA*=Val, Leu, Thr, Arg, Phe and Try) have been prepared in 95% alcoholic, the compositions of which were identified as the general formula $Cr(AA)_2(NO_3)_3\cdot 2H_2O$ by elemental and chemical analyses. The bonding characteristics of the title complexes were characterized by IR, indicating that nitrogen and oxygen atoms in the ligands coordinated to $Cr^{3+}$ in a bidentate fashion. With the aid of TG-DTG and IR techniques, the complexes were subjected to thermal decomposition in an atmosphere of oxygen, presuming that the decompositions of the complexes consist of two steps and the complexes were decomposed into chromium hemitrioxide after undergoing dehydration and skeleton splitting of the complexes. The constant volume energies of combustion of the complexes were determined by a RBC-Π type rotating-bomb calorimeter. According to Hess's law, the standard enthalpies of formation of the complexes were calculated as (–1831.40±4.40), (–2542.03±6.13), (–1723.81±3.99), (–2224.31±3.02), (–2911.61±6.53) and (–659.32±7.42) kJ $mol^{-1}$, respectively.

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

## Introduction

GTF, the indispensable cofactor of insulin, is a complex by amino acid and niacin coordination to microelement-chromium. Insulin does not keep the normal sugar metabolic unless GTF has affinity for its complexity [1]. *L*-α-amino acids are structural unit of protein, especially for Val, Leu, Thr, Arg, Phe and Try, which are essential to life and have to be absorbed from foods due to being not synthesized by organism. It is not surprising that a good understanding of coordination behavior of chromium with amino acids is basic to acquaintance with GTF. So, there is considerable practical and fundamental importance to focus on the complex of chromium and amino acids.

Regarding the complexes of chromium with valine, leucin, methionine and phenylalanine, the properties on spectrum, NMR and magnetism in mixture solvent

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of water with alcohol have been reported [2–8]. It has been studied by Cooper on the structure, biological activity, chromatography, spectrum for the complexes of chromium with amino acids in the mole ratio of chromium to amino acid 1:2 and the relationship between the complexes and GTF [1]. Our research group [9] investigated the solubility property of the ternary of $Cr(NO_3)_3$–His–$H_2O$, disclosed the existence of the new solid complexes of $Cr(His)(NO_3)_3\cdot 3H_2O$(A), $Cr(His)_2(NO_3)_3\cdot 3H_2O$ (B) and $Cr(His)_3(NO_3)_3\cdot 3H_2O$ (C), determined the enthalpy of the reaction of $Cr(NO_3)_3$ with histidine as well as calculated thermokinetic parameters and thermodynamic parameters. In our present work, six solid complexes of $Cr(AA)_2(NO_3)_3\cdot 2H_2O$ of $Cr(NO_3)_3$ with *L*-α-amino acids (*AA*=Val, Leu, Thr, Arg, Phe and Try) have been prepared in 95% alcoholic and characterized by chemical analysis, elemental analysis, IR and TG-DTG techniques. The constant-volume energies of combustion of these complexes were determined by a RBC-Π-type rotating-bomb calorimeter, and the standard enthalpies of formation of these complexes were calculated as well. Obviously, this work enriches the thermochemical database and provides a theoretical basis for new applications of the title complexes.

## Experimental

### *Preparations and compositions of the complexes*

$Cr(NO_3)_3\cdot 9H_2O$ and L-α-amino acids were blended with the molar ratio of 1:2 in 95% alcoholic. After refluxing on 70–80°C water bath for 6 h, the solution was condensed to remove a large amount of alcoholic, filtered and the aim products are obtained and identified as $Cr(Val)_2(NO_3)_3\cdot 2H_2O$ (A), $Cr(Leu)_2(NO_3)_3\cdot 2H_2O$ (B), $Cr(Thr)_2(NO_3)_3\cdot 2H_2O$ (C), $Cr(Arg)_2(NO_3)_3\cdot 2H_2O$ (D), $Cr(Phe)_2(NO_3)_3\cdot 2H_2O$ (E) and $Cr(Try)_2(NO_3)_3\cdot 2H_2O$ (F) by chemical and elemental analyses. $Cr(NO_3)_3\cdot 9H_2O$ (Beijing Hongxing Chemical Plant, A.R.) and *L*-α-amino acids were recrystallized with the purity of 99.95%. The purity of the complexes is greater than to 99.99% checked by HPLC. The analytical results on the compositions of the complexes are summarized in Table 1.

### Apparatus and experimental procedures

It is a RBC-Π-type rotating-bomb calorimeter by which the constant-volume energy of combustion of the complex was determined [10]. Based on a RBC-Π-type rotating-bomb [11], a RBC-Π-type rotating-bomb with digital indicator wherein integrated circuit was employed, aiming at promoting the precision and accurate of the experimental thermochemistry, was developed. The accurate uncertainty of the present calorimeter has been reduced from $1.6\cdot 10^{-3}$ to $4.68\cdot 10^{-4}$ by calibration for the standard benzoic acid of purity of 99.999%. Benzoic acid has an isothermal heat of combustion at 25°C of –26434 J $g^{-1}$. The calibrated experimental results are presented in Table 2. The calibration for the apparatus and temperature, the determination processes of the experiment as well as the analyses of final products are identical with [10].

**Table 1** Analytical results of compositions of complexes (%)*

| Complex | $Cr^{3+}$ | C | H | N |
|---|---|---|---|---|
| A | 10.30 (10.23) | 23.69 (23.63) | 5.18 (5.16) | 13.74 (13.78) |
| B | 9.54 (9.69) | 26.92 (26.87) | 5.69 (5.64) | 13.02 (13.06) |
| C | 10.03 (10.15) | 18.79 (18.76) | 4.38 (4.33) | 13.62 (13.67) |
| D | 8.32 (8.35) | 23.19 (23.16) | 5.22 (5.18) | 24.72 (24.75) |
| E | 8.51 (8.60) | 35.84 (35.77) | 4.39 (4.34) | 11.54 (11.59) |
| F | 7.72 (7.62) | 38.85 (38.72) | 4.18 (4.149 | 14.32 (14.37) |

*$Cr^{3+}$ is determined complexometrically with ammonium ferrous sulfate.
Carbon, hydron and nitrogen analyses are performed on a 2400 – type elemental analyzer of PE company.
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 % $q_c$/J | Calibrated heat of acid containing nitrogen $q_N$/J | Calibrated $\Delta T$/K | Energy equivalent of calorimeter $W$/J $K^{-1}$ |
|---|---|---|---|---|---|
| 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 | | | | | 18007.71 8.42 |

The IR spectra of the compounds were run on a Bruker EQ UINOX-550 model infrared spectrophotometer, within the range 4000–400 $cm^{-1}$ range and the solid samples were pressed into KBr pellets. 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. Carbon and hydrogen contents were determined by microanalytical procedures, with a 2400-type elemental analyzer from PE instrument.

## Results and discussion

### *IR spectra of the complexes*

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

**Table 3** Data of IR absorption for main groups of ligands and complexes (cm$^{-1}$)

| Comp. | $\nu^{as}_{NH_3^+}$<br>$\nu^{as}_{NH_2}$ | $\nu^{s}_{NH_3^+}$<br>$\nu^{s}_{NH_2}$ | $\delta^{as}_{NH_3^+}$<br>$\delta^{as}_{NH_2}$ | $\delta^{s}_{NH_3^+}$<br>$\delta^{s}_{NH_2}$ | $\nu^{as}_{COO^-}$ | $\nu^{s}_{COO^-}$ | $\nu_{OH}$ | $\nu_{OH}$ | $\nu_{COH}$ | $\nu_{C_6H_5}$ | $\nu^{as}_{CCN}$ | $\nu^{s}_{CCN}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Val | 3455 | 2977 | 1615 | 1506 | 1600 | 1426 | – | – | – | – | – | – |
| Leu | 3454 | 2958 | 1613 | 1514 | 1583 | 1407 | – | – | – | – | – | – |
| Thr | 3441 | 2959 | 1627 | 1456 | 1564 | 1417 | – | – | 1107 | – | – | – |
| Arg | 3301 | 3097 | 1683 | 1561 | 1614 | 1420 | – | – | – | – | – | – |
| Phe | 3028 | 2130 | 1629 | 1496 | 1567 | 1413 | – | – | – | 1074 | – | – |
| Try | 3404 | 3038 | 1667 | 1456 | 1591 | 1357 | – | – | – | – | 1315 | 743 |
| A | 3091 | 2973 | 1657 | 1453 | 1522 | 1384 | 3409 | 824 | – | – | – | – |
| B | 3091 | 2963 | 1662 | 1458 | 1523 | 1385 | 3409 | 825 | – | – | – | – |
| C | 3080 | 2979 | 1664 | 1384 | 1508 | 1384 | 3410 | 825 | 1111 | – | – | – |
| D | 3205 | 2977 | 1655 | 1453 | 1633 | 1350 | 3409 | 826 | – | – | – | – |
| E | 3031 |  | 1662 | 1457 | 1522 | 1585 | 3398 | 823 | – | 1081 | – | – |
| F | 3057 | 2973 | 1658 | 1457 | 1509 | 1385 | 3407 | 823 | – | – | 1319 | 744 |

- To the complexes, the characteristic absorption peaks of amino and carboxyl groups have a great shift as compared to those in the free ligand. It indicated that nitrogen and oxygen atoms in the complexes coordinate to $Cr^{3+}$ in a bidentate fashion.
- The characteristic absorption peaks of hydroxyl, benzol and indolyl group in the complexes have a little shift compared with the related ligands of Thr, Phe and Try, which is attributable to the environment effect. It is confirmed that the hydroxyl, benzol and indolyl groups do not participate in coordination to chromium.
- The characteristic absorption of 3390–3423 and 823–828 $cm^{-1}$ in the complexes are assigned to that of water, which is evidence for the presence of water molecule in the complexes.

### *Thermostability of the complexes*

The TG-DTG curves of the complexes are presented in Fig. 1. The appearance of peaks in the TG-DTG curves suggested that the thermal decompositions of the complexes consist of two steps. For the complex of A–C, the first stage start at 51°C and complete at 335, 300 and 279°C, accompanying with 53.35, 55.50 and 53.46% mass loss. There are in good agreement with the calculated value of the mass loss of 53.17, 55.62 and 53.53%, corresponding to the skeleton splitting of the complexes. In the second step of 300–522°C, the skeletons of the complexes are further splitted, and the complexes completely collapse and transformed into the final product. This process proceeded with 31.44, 30.18 and 32.05% mass loss, which coincide with the calculated value of the mass loss 31.88, 30.21 and 31.63%, preliminarily showing the final product is chromium hemitrioxide. In order to

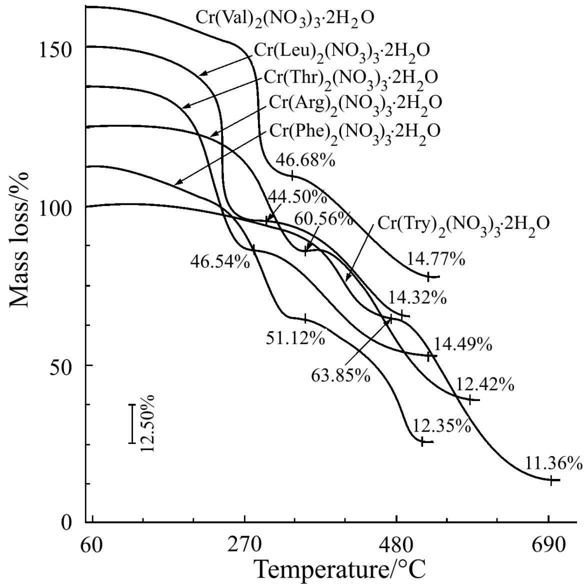

**Fig. 1** TG curves for the complexes in an atmosphere of oxygen

acquire insight into the decomposition pathway for the complexes of A–C, decomposition–interruption tests were conducted with TG-DTG experiments and the infrared analyses of the residual matter before and after thermal decomposition were performed. The experimental results show that, the IR spectrum of the final product is identical with that of the standard spectrum $Cr_2O_3$ when IR spectrum of the residual products after the first stages fit with that of $Cr(NO_3)_3$ [14].

**Table 4** Thermoanalytical results of the complexes

| Complex | Decomposition product | Decomposition temp./°C | Residual rate/% |
|---|---|---|---|
| A | $Cr(NO_3)_3$ | 51–298–335$^a$ | 46.65 (46.83)$^b$ |
| | $Cr_2O_3$ | 335–411–522 | 14.77 (14.95) |
| B | $Cr(NO_3)_3$ | 51–270–300 | 44.50 (44.38) |
| | $Cr_2O_3$ | 300–373–488 | 14.32 (14.17) |
| C | $Cr(NO_3)_3$ | 51–256–279 | 46.54 (46.47) |
| | $Cr_2O_3$ | 279–399–522 | 14.49 (14.84) |
| D | $2Cr(Arg)_2(NO_3)_3\ 3Cr(NO_3)_3$ | 51–304–353 | 60.56 (60.63) |
| | $Cr_2O_3$ | 353–387–577 | 12.42 (12.21) |
| E | $2Cr(Phe)_2(NO_3)_3\ 7Cr(NO_3)_3$ | 51–250–350 | 51.12 (51.53) |
| | $Cr_2O_3$ | 350–457–512 | 12.53 (12.58) |
| F | $9Cr(Try)_2(NO_3)_3\ 10Cr(NO_3)_3$ | 51–377–474 | 63.85 (63.22) |
| | $Cr_2O_3$ | 474–547–696 | 11.36 (11.14) |

As to the complexes of D–F, the first decomposition steps begin at 51°C and end at 353, 350 and 474°C with the observed mass losses of 39.44, 48.88 and 36.15%, respectively, when the calculated values are 39.37, 48.47 and 36.78%. The corresponding mass losses are due to the decomposition of the partial removal of the ligands of Arg, Phe and Try. IR analyses show that the spectrum of the residual product are identified as overlapping spectrum of the compounds of $Cr(NO_3)_3$ and $Cr(AA)_2(NO_3)_3$ (*AA*=Arg, Phe and Try). The final stages occur at 470–700°C, accompanying with the mass loss of 48.36, 38.59 and 52.49% which comply with the calculated value of 48.42, 38.95 and 52.08%. The final product corresponds to the compound of $Cr_2O_3$ as confirmed by IR analysis [14].

In accordance with the IR spectra and TG-DTG experiments described above, it is assumed that the thermal decomposition processes for the complexes are summarized in Table 4.

### *The constant volume energy of combustion and standard enthalpy of formation for the complexes*

The constant-volume energies of combustion of the complexes determined by a RBC-Π-type rotating-bomb calorimeter are summarized in Table 5.

**Table 5** The experimental results for the energies of combustion of the complexes

| Comp. | No. | Mass of sample, *a*/g | Calibrated heat of combustion wire, $q_c$/J | Calibrated heat of acid cont. nitrogen, $q_N$/J | Calibr. $\Delta T$/K | Combustion energy of samples, $-\Delta_{c,\,coor}E$/J g$^{-1}$ |
|---|---|---|---|---|---|---|
| A | 1 | 1.06737 | 12.60 | 176.77 | 0.7577 | 12600.85 |
| | 2 | 1.10021 | 11.70 | 182.21 | 0.7786 | 12562.55 |
| | 3 | 1.00536 | 12.60 | 166.50 | 0.7115 | 12560.54 |
| | 4 | 0.99285 | 12.60 | 164.43 | 0.7052 | 12607.21 |
| | 5 | 0.99587 | 9.90 | 164.93 | 0.7064 | 12592.88 |
| | 6 | 1.00029 | 12.60 | 165.66 | 0.7086 | 12573.40 |
| | mean | | | | | 12582.91 8.20 |
| B | 1 | 0.85636 | 12.60 | 72.09 | 0.7036 | 14690.80 |
| | 2 | 0.91274 | 12.60 | 76.83 | 0.7496 | 14685.34 |
| | 3 | 0.87510 | 11.70 | 73.66 | 0.7180 | 14671.64 |
| | 4 | 0.88476 | 10.80 | 74.48 | 0.7273 | 14700.75 |
| | 5 | 0.84698 | 12.60 | 71.30 | 0.6948 | 14667.40 |
| | 6 | 0.88720 | 12.60 | 74.68 | 0.7289 | 14690.53 |
| | mean | | | | | 14684.41 5.15 |
| C | 1 | 1.20536 | 12.60 | 168.47 | 0.6837 | 10060.08 |
| | 2 | 1.15430 | 11.70 | 161.33 | 0.6539 | 10047.84 |
| | 3 | 1.16722 | 12.60 | 163.14 | 0.6600 | 10027.87 |
| | 4 | 1.17089 | 12.60 | 163.65 | 0.6647 | 10068.26 |
| | 5 | 1.05424 | 12.60 | 147.35 | 0.5990 | 10075.86 |
| | 6 | 1.11540 | 12.60 | 155.90 | 0.6314 | 10038.68 |
| | mean | | | | | 10053.10 7.46 |
| D | 1 | 0.98526 | 12.60 | 108.91 | 0.6803 | 12305.76 |
| | 2 | 0.99360 | 11.70 | 109.83 | 0.6857 | 12300.28 |
| | 3 | 0.98394 | 10.80 | 108.76 | 0.6782 | 12285.83 |
| | 4 | 1.00357 | 12.60 | 110.95 | 0.6914 | 12287.33 |
| | 5 | 1.01062 | 12.60 | 111.71 | 0.6970 | 12291.65 |
| | 6 | 0.99436 | 12.60 | 109.92 | 0.6859 | 12293.50 |
| | mean | | | | | 12292.56 4.01 |
| E | 1 | 1.00156 | 11.70 | 104.86 | 0.7857 | 14004.75 |
| | 2 | 0.99630 | 12.60 | 104.36 | 0.7828 | 14025.94 |
| | 3 | 0.98725 | 12.60 | 103.36 | 0.7736 | 13987.73 |
| | 4 | 0.98841 | 9.90 | 103.48 | 0.7748 | 13995.78 |

**Table 5** Continued

| Comp. | No. | Mass of sample, $a$/g | Calibrated heat of combustion wire, $q_c$/J | Calibrated heat of acid cont. nitrogen, $q_N$/J | Calibr. $\Delta T$/K | Combustion energy of samples, $-\Delta_{c,\ coor}E$/J g$^{-1}$ |
|---|---|---|---|---|---|---|
| E | 5 | 1.01548 | 12.60 | 106.32 | 0.7947 | 13969.99 |
| | 6 | 1.03069 | 12.60 | 107.91 | 0.8104 | 14036.49 |
| | mean | | | | | 14003.45 10.04 |
| F | 1 | 0.88450 | 12.60 | 165.34 | 0.9165 | 18450.78 |
| | 2 | 0.85220 | 12.60 | 159.30 | 0.8809 | 18405.22 |
| | 3 | 0.90026 | 11.70 | 168.29 | 0.9302 | 18399.43 |
| | 4 | 0.86532 | 10.80 | 161.75 | 0.8970 | 18460.32 |
| | 5 | 0.86835 | 12.60 | 162.32 | 0.8990 | 18434.64 |
| | 6 | 0.85478 | 12.60 | 159.78 | 0.8843 | 18420.70 |
| | mean | | | | | 18428.52 9.99 |

The standard enthalpies of combustion of the complexes, $\Delta_{c,coor}H_m^\theta$, refer to the enthalpy changes of combustion of the following ideal combustion reactions at 298.15 K and 101.325 kPa.

$$\begin{gathered}\mathrm{Cr(Val)_2(NO_3)_3{\cdot}2H_2O}(s)+39/4\mathrm{O_2}\,(g)= \\ =1/2\mathrm{Cr_2O_3}\,(s)+10\mathrm{CO_2}\,(g)+13\mathrm{H_2O}\,(l)+5/2\mathrm{N_2}\,(g)\end{gathered} \tag{1}$$

$$\begin{gathered}\mathrm{Cr(Leu)(NO_3)_3{\cdot}2H_2O}(s)+51/4\mathrm{O_2}\,(g)= \\ =1/2\mathrm{Cr_2O_3}(s)+12\mathrm{CO_2}(g)+15\mathrm{H_2O}(l)+5/2\mathrm{N_2}\,(g)\end{gathered} \tag{2}$$

$$\begin{gathered}\mathrm{Cr(Thr)_2(NO_3)_3{\cdot}2H_2O}(s)+23/4\mathrm{O_2}\,(g)= \\ =1/2\mathrm{Cr_2O_3}(s)+8\mathrm{CO_2}\,(g)+11\mathrm{H_2O}(l)+7/2\mathrm{N_2}\,(g)\end{gathered} \tag{3}$$

$$\begin{gathered}\mathrm{Cr(Arg)\ (NO_3)_3{\cdot}2H_2O}(s)+53/4\mathrm{O_2}\,(g)= \\ =1/2\mathrm{Cr_2O_3}(s)+12\mathrm{CO_2}(g)+16\mathrm{H_2O}(l)+11/2\mathrm{N_2}\,(g)\end{gathered} \tag{4}$$

$$\begin{gathered}\mathrm{Cr(Phe)_2(NO_3)_3{\cdot}2H_2O}(s)+71/4\mathrm{O_2}(g)= \\ =1/2\mathrm{Cr_2O_3}\,(s)+18\mathrm{CO_2}(g)+13\mathrm{H_2O}(l)+5/2\mathrm{N_2}\,(g)\end{gathered} \tag{5}$$

$$\begin{gathered}\mathrm{Cr(Try)_2(NO_3)_3{\cdot}2H_2O}(s)+89/4\mathrm{O_2}(g)= \\ =1/2\mathrm{Cr_2O_3}(s)+10\mathrm{CO_2}(g)+13\mathrm{H_2O}(l)+5/2\mathrm{N_2}\,(g)\end{gathered} \tag{6}$$

The standard enthalpies of combustion of the complexes are calculated from the energies of combustion by the Eqs (1)–(6).

$$\Delta_{c,coor}H_m^\theta=\Delta_{c,coor}E+\Delta nRT \tag{7}$$

where, $n_{gas}$ represents the total amount (in moles) of gas present as products or as reactants, $R$=8.314 J mol$^{-1}$ K$^{-1}$, $T$=298.15 K. The results of the calculations are also shown in Table 6.

**Table 6** Energies of combustion, standard enthalpies of combustion and standard enthalpies of formation for the complexes (kJ mol$^{-1}$)

| Complex | $-\Delta_{\mathrm{c,\,coor}}E$ | $-\Delta_{\mathrm{c,\,coor}}H^{\theta}_{\mathrm{m}}$ | $-\Delta_{\mathrm{f,\,coor}}H^{\theta}_{\mathrm{m}}$ |
|---|---|---|---|
| A | 6396.36 4.17 | 6389.54 4.17 | 1831.20 4.40 |
| B | 12252.31 5.73 | 12249.83 5.73 | 2542.03 6.13 |
| C | 5150.02 3.82 | 5138.25 3.82 | 1723.81 3.99 |
| D | 7651.47 2.50 | 7640.94 2.50 | 2224.31 3.02 |
| E | 8464.03 6.07 | 8457.21 6.07 | 2911.61 6.53 |
| F | 12577.43 6.82 | 12569.37 6.82 | 659.32 7.42 |

The standard enthalpies of formation of the complexes, $\Delta_{\mathrm{f,coor}}H^{\theta}_{\mathrm{m}}$, are calculated by Hess's law according to the thermochemical Eqs (1)–(6).

$$\Delta_{\mathrm{f,A(s)}}H^{\theta}_{\mathrm{m}}=[0.5\Delta_{\mathrm{f,Cr_2O_3(s)}}H^{\theta}_{\mathrm{m}}+10\Delta_{\mathrm{f,CO_2(g)}}H^{\theta}_{\mathrm{m}}+13\Delta_{\mathrm{f,H_2O(l)}}H^{\theta}_{\mathrm{m}}]-\Delta_{\mathrm{c,A(s)}}H^{\theta}_{\mathrm{m}} \tag{8}$$

$$\Delta_{\mathrm{f,B(s)}}H^{\theta}_{\mathrm{m}}=[0.5\Delta_{\mathrm{f,Cr_2O_3(s)}}H^{\theta}_{\mathrm{m}}+12\Delta_{\mathrm{f,CO_2(g)}}H^{\theta}_{\mathrm{m}}+15\Delta_{\mathrm{f,H_2O(l)}}H^{\theta}_{\mathrm{m}}]-\Delta_{\mathrm{c,B(s)}}H^{\theta}_{\mathrm{m}} \tag{9}$$

$$\Delta_{\mathrm{f,C(s)}}H^{\theta}_{\mathrm{m}}=[0.5\Delta_{\mathrm{f,Cr_2O_3(s)}}H^{\theta}_{\mathrm{m}}+8\Delta_{\mathrm{f,CO_2(g)}}H^{\theta}_{\mathrm{m}}+11\Delta_{\mathrm{f,H_2O(l)}}H^{\theta}_{\mathrm{m}}]-\Delta_{\mathrm{c,C(s)}}H^{\theta}_{\mathrm{m}} \tag{10}$$

$$\Delta_{\mathrm{f,D(s)}}H^{\theta}_{\mathrm{m}}=[0.5\Delta_{\mathrm{f,Cr_2O_3(s)}}H^{\theta}_{\mathrm{m}}+12\Delta_{\mathrm{f,CO_2(g)}}H^{\theta}_{\mathrm{m}}+16\Delta_{\mathrm{f,H_2O(l)}}H^{\theta}_{\mathrm{m}}]-\Delta_{\mathrm{c,D(s)}}H^{\theta}_{\mathrm{m}} \tag{11}$$

$$\Delta_{\mathrm{f,E(s)}}H^{\theta}_{\mathrm{m}}=[0.5\Delta_{\mathrm{f,Cr_2O_3(s)}}H^{\theta}_{\mathrm{m}}+18\Delta_{\mathrm{f,CO_2(g)}}H^{\theta}_{\mathrm{m}}+13\Delta_{\mathrm{f,H_2O(l)}}H^{\theta}_{\mathrm{m}}]-\Delta_{\mathrm{c,E(s)}}H^{\theta}_{\mathrm{m}} \tag{12}$$

$$\Delta_{\mathrm{f,F(s)}}H^{\theta}_{\mathrm{m}}=[0.5\Delta_{\mathrm{f,Cr_2O_3(s)}}H^{\theta}_{\mathrm{m}}+22\Delta_{\mathrm{f,CO_2(g)}}H^{\theta}_{\mathrm{m}}+14\Delta_{\mathrm{f,H_2O(l)}}H^{\theta}_{\mathrm{m}}]-\Delta_{\mathrm{c,F(s)}}H^{\theta}_{\mathrm{m}} \tag{13}$$

where $\Delta_{\mathrm{f,\,Cr_2O_3(s)}}H^{\theta}_{\mathrm{m}}=-1139.70$ kJ mol$^{-1}$, $\Delta_{\mathrm{f,\,Co_2(g)}}H^{\theta}_{\mathrm{m}}=(-393.51\pm0.13)$ kJ mol$^{-1}$, $\Delta_{\mathrm{f,\,H_2O(l)}}H^{\theta}_{\mathrm{m}}=(-285.83\pm0.042)$ kJ mol$^{-1}$ [15]. The energies of combustion, the standard enthalpies of combustion and the standard enthalpies of formation of the complexes are presented in Table 6. Obviously, the standard enthalpies of formation of the complexes vary with the structures of amino acids.

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