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Thermochemistry on $K_2[M(DPA)_2]\cdot 7H_2O(s)$ (M = Cu and Ni, H_2DPA = pyridine-2,6-dicarboxylic acid)

Guo-Chun Zhang [a,b], San-Ping Chen [a,*], Qi Yang [a], Sheng-Li Gao [a,*]

[a] Key Laboratory of Synthetic and Natural Functional Molecule Chemistry of Ministry of Education, College of Chemistry & Materials Science, Northwest University, Xi'an, Shaanxi 710069, PR China
[b] Department of Chemistry & Chemical Engineering, Shangluo University, Shangzhou, Shaanxi 726000, PR China

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ABSTRACT

Two hybrid transition-alkali metal complexes, $K_2[M(DPA)_2]\cdot 7H_2O(s)$ (M = Cu and Ni, H_2DPA = pyridine-2,6-dicarboxylic acid), were structurally determined by X-ray crystallography. In accordance with Hess's law, two reasonable thermochemical cycles were designed and 100 cm^3 of 5% (v/v) dilute aquaammonia was chosen as the calorimetric solvent. The standard molar enthalpies of dissolution for the reactants and products of the supposed reactions in the selected solvent were measured at 298.15 K by means of isoperibol solution-reaction calorimeter, respectively. The standard molar enthalpies of formation of $K_2[M(DPA)_2]\cdot 7H_2O(s)$ (M = Cu and Ni) were derived to be $-(3947.7 \pm 4.7)$ kJ mol^{-1} and $-(4007.8 \pm 4.7)$ kJ mol^{-1}, respectively.

1. Introduction

It is well-known that nickel and copper are two of the trace elements necessary for human, animal and plant. They have the important physiological functions and nutritional values, and participate in many metabolic processes of the cells in the biological body. The nickel-deficiency may reduce the activation of the insulin, hinder the utilization of sugar in the human body, increase the content of fat and lipoid in blood, which may deposit the fat and lipoid in the wall of blood vessel, cause the arterial atherosclerosis, and finally result in hypertension, sugar diabetes and cardiovascular diseases and so on. Copper is intimately related to more than 300 kinds of the enzymes in the human body and promotes growth and development of the issues. The cupric-deficiency may result in many kinds of diseases, including sugar diabetes, cardiovascular diseases and so on. Pyridine-2,6-dicarboxylic acid (H_2DPA) has a recognized biological function in the body metabolism. It has the ability to build stabilizing structures with divalent metals [1] and also can form bridging hydrogen bonds making it useful for self-assembly.

Nathan and Mai [2] had synthesized $K_2[Ni(DPA)_2]\cdot 7H_2O(s)$ using potassium hydroxide and appropriate hydrated metal acetate in acetone/water. They investigated the crystal structure of the complex with X-ray crystallography. By comparison, it can be seen that the crystal structure of the complex looks similar to reported in the literature [2]. We have not found the crystal structure of $K_2[Cu(DPA)_2]\cdot 7H_2O(s)$ in the literature. However, up to now, the thermodynamic properties (such as standard molar enthalpy of formation) of the two complexes have not been found in the literature. Enthalpy of dissolution and standard molar enthalpy of formation of a substance are important data in calculating enthalpy changes and theoretical yields of reactions in which the substance is involved. In the present work, the standard molar enthalpies of $K_2[M(DPA)_2]\cdot 7H_2O(s)$ (M = Cu and Ni) were derived by means of isoperibol solution-reaction calorimeter, respectively.

2. Experimental

2.1. Synthesis of $K_2[M(DPA)_2]\cdot 7H_2O(s)$ (M = Cu and Ni)

The mixture of $Cu(Ac)_2\cdot H_2O$ (2 mmol), KOH (4 mmol) and H_2DPA (4 mmol) were added into distilled water (40 cm^3) slowly. The mixture solution was stirred and refluxed for 6 h, and cooled to room temperature. The resulting blue solution was filtered and left to yield blue crystal. Theoretical contents of C, H, N, K and Cu in the complex have been calculated to be 28.12%, 3.37%, 4.68%, 13.08% and 10.63%, respectively. Chemical and elemental analysis (model: PE-2400, PerkinElmer, USA) have shown that the practical contents

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* Corresponding authors. Tel.: +86 29 88302604; fax: +86 29 88303798.
E-mail addresses: sanpingchen@126.com (S.-P. Chen), gaoshli@nwu.edu.cn (S.-L. Gao).

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Table 1
Crystallographic data and structure refinements for the title compounds.

Empirical formula	$C_{14}H_{20}CuK_2N_2O_{15}$	$C_{14}H_{20}NiK_2N_2O_{15}$
Formula weight	598.06	593.23
Wavelength (Å)	0.71073	0.71073
Crystal system	Orthorhombic	Orthorhombic
space group	Pnna (No. 52)	Pnna (No. 52)
a (Å)	20.838(2)	20.678(2)
b (Å)	13.3910(14)	13.4021(15)
c (Å)	8.1824(8)	8.2525(13)
α (°)	90	90
β (°)	90	90
γ (°)	90	90
Volume (Å^3)	2283.3(4)	2287.0(5)
Z	4	4
Calculated density (g cm^{-3})	1.740	1.723
Absorption coefficient (mm^{-1})	1.398	1.289
F(0 0 0)	1220	1216
θ range for data collection (°)	1.95–25.01	1.97–25.01
Data/restraints/ parameters	2029/0/157	2031/0/156
Goodness-of-fit on F^2	1.039	1.075
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0349$, $wR_2 = 0.0864$	$R_1 = 0.0328$, $wR_2 = 0.0751$
R indices (all data)	$R_1 = 0.0491$, $wR_2 = 0.0981$	$R_1 = 0.0498$, $wR_2 = 0.0867$
Largest diff. peakand hole (e Å^{-3})	0.508 and −0.447	0.427 and −0.453

of C, H, N, K and Cu in the complex were measured to be 27.98%, 3.35%, 4.66%, 13.04% and 10.60%, respectively.

$Ni(Ac)_2 \cdot 4H_2O$ (2 mmol) was added to a mixture of KOH (8 mmol) and H_2DPA (4 mmol) in a mixed solvent of distilled water (15 cm^3) and methanol (15 cm^3) slowly. The mixture solution was stirred and refluxed for 6 h, and cooled to room temperature. The resulting green solution was filtered and left to yield blue crystal. Theoretical contents of C, H, N, K and Ni in the complex have been calculated to be 28.35%, 3.40%, 4.72%, 13.18% and 9.89%, respectively. Chemical and elemental analysis (model: PE-2400, PerkinElmer, USA) have shown that the practical contents of C, H, N, K and Ni in the complex were measured to be 28.31%, 3.37%, 4.70%, 13.14% and 9.85%, respectively.

2.2. X-ray crystallography

Two crystals with suitable dimensions were glued to fine glass fiber and then mounted on the Bruker Smart-1000 CCD diffractometer with Mo-Kα radiation, $\lambda = 0.071073$ nm. The intensity data were collected at 298(2) K in the φ–ω scan mode. The structures were solved by direct methods and expanded using Fourier techniques with SHELXL-97 program [3]. The non-hydrogen atoms were refined anisotropically by full-matrix least-squares calculations on F^2 using the SHELXTL-97 program. The hydrogen atoms were added theoretically, riding on the concerned atoms and not refined.

2.3. Isoperibol solution-reaction calorimetry

The isoperibol solution-reaction calorimeter consisted primarily of a precision temperature control system, an electric energy calibration system, a calorimetric body, an electric stirring system, a thermostatic bath made from transparent silicate glass, a precision temperature measuring system, and a data acquisition system.

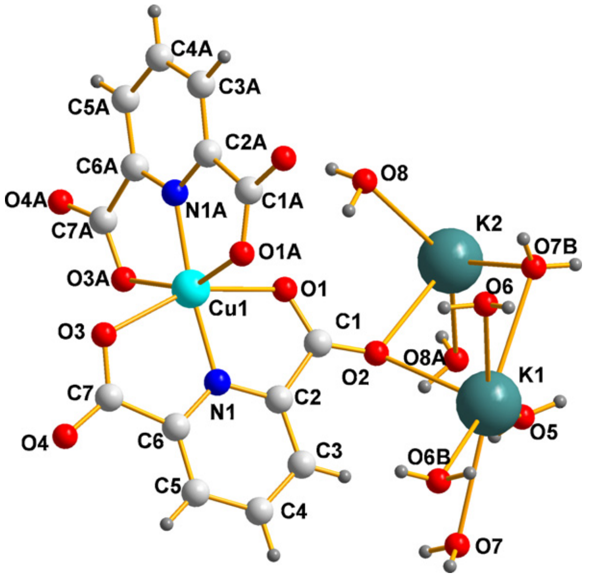

Fig. 1. Molecular structure of the compound $K_2[Cu(DPA)_2] \cdot 7H_2O(s)$.

The principle and structure of the calorimeter were described in detail elsewhere [4].

The reliability of the calorimeter was verified previously [4] by measuring the dissolution enthalpy of KCl (calorimetrically primary standard) in double distilled water at $T = 298.15$ K. The mean dissolution enthalpy was $17{,}547 \pm 13$ J mol^{-1} for KCl, which compared with corresponding published data, $17{,}536 \pm 3.4$ J mol^{-1} [5].

3. Results and discussion

3.1. Crystal structures of $K_2[M(DPA)_2] \cdot 7H_2O(s)$ (M = Cu and Ni)

All the detail crystal data are listed in Table 1. The crystal structures of the two compounds are both orthorhombic, the space groups are both Pnna and $Z = 4$. The unit cell dimensions of $K_2[M(DPA)_2] \cdot 7H_2O(s)$ (M = Cu and Ni) are very close, for $K_2[Cu(DPA)_2] \cdot 7H_2O(s)$, $a = 2.0838(2)$ nm, $b = 1.33910(14)$ nm, $c = 0.81824(8)$ nm, $\alpha = \beta = \gamma = 90°$; for $K_2[Ni(DPA)_2] \cdot 7H_2O$ (s), $a = 2.0678(2)$ nm, $b = 1.34021(15)$ nm, $c = 0.82525(13)$ nm, $\alpha = \beta = \gamma = 90°$.

Fig. 1 shows the molecular structure of $K_2[Cu(DPA)_2] \cdot 7H_2O(s)$. The cupric(II) cation is coordinated by two N atoms and four O atoms from two pyridine-2,6-dicarboxylic acid forming a slightly distorted octahedron geometry with two N atoms of two pyridine-2,6-dicarboxylic acid at the apical position. Cu(1)–O(1) = 0.2168 nm, Cu(1)–O(1A) = 0.2168 nm; Cu(1)–O(3) = 0.2208 nm, Cu(1)–O(3A) = 0.2208 nm. The bond length of Cu(1)–O(1) and Cu(1)–O(1A) are slightly shorter than Cu(1)–O(3) and Cu(1)–O(3A). The difference may be caused by steric hindrance around the O atom. The K(I) and Cu(II) cations were connected by carboxyl group of pyridine-2,6-dicarboxylic acid. The distance of K–O is between 0.26 and 0.29 nm, which is all weak coordination bond. In addition, the O_2 of pyridine-2,6-dicarboxylic acid and O7B of water molecules as coordination connect K(1) and K(2). The complex is a three-dimensional network of infinite length connection with crystal waters, potassium ions and hydrogen bonds.

Fig. 2 shows the molecular structure of $K_2[Ni(DPA)_2] \cdot 7H_2O(s)$. $K_2[Ni(DPA)_2] \cdot 7H_2O(s)$ and $K_2[Cu(DPA)_2] \cdot 7H_2O(s)$ are isostructural. In addition, the parameters of crystal structure of $K_2[Ni(DPA)_2] \cdot 7H_2O(s)$ are similar to the literature [2].

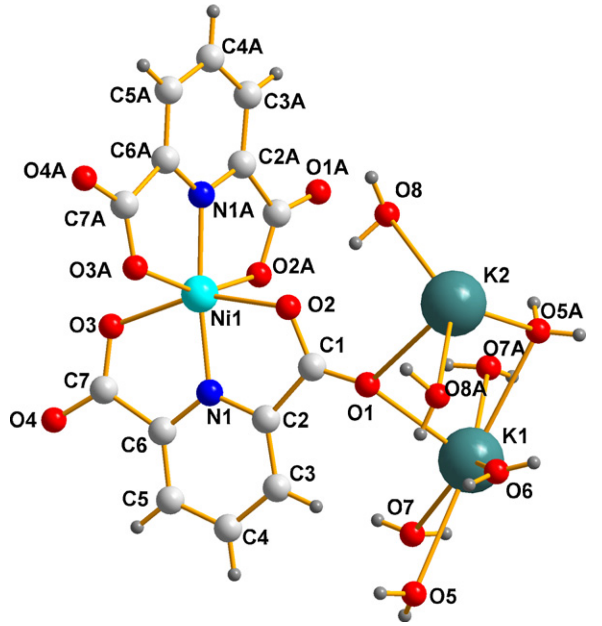

Fig. 2. Molecular structure of the compound $K_2[Ni(DPA)_2]{\cdot}7H_2O(s)$.

3.2. Determination of enthalpies change for the two reactions

The two supposed reactions are expressed as followed:

$$2H_2DPA(s) + Cu(Ac)_2 \cdot H_2O(s) + 2KAc(s) + 6H_2O(1) = K_2[Cu(DPA)_2] \cdot 7H_2O(s) + 4HAc(l) \qquad (1)$$

$$2H_2DPA(s) + Ni(Ac)_2 \cdot 4H_2O(s) + 2KAc(s) + 3H_2O(1) = K_2[Ni(DPA)_2] \cdot 7H_2O(s) + 4HAc(l) \qquad (2)$$

The enthalpy changes of reactions (1) and (2) can be determined, respectively, by measuring the enthalpies of dissolution of reactants and products in 5% (v/v) dilute aquaammonia at 298.15 K.

About 0.0005 mol or 0.08 g of $H_2DPA(s)$ was dissolved in 100 cm^3 of 5% (v/v) dilute aquaammonia at 298.15 K. If “s” = calorimetric solvent (5%, v/v, dilute aquaammonia), then $H_2DPA(s)$ + “s” = solution A‴. The results obtained from five dissolution experiments are listed in Table 2.

The stoichiometric number of $Cu(Ac)_2{\cdot}H_2O(s)$ in the reaction (1) or [n $(H_2DPA)/(Cu(Ac)_2{\cdot}H_2O)$ = 2:1] was regarded as a norm for sample weighing, about 0.05 g $Cu(Ac)_2{\cdot}H_2O(s)$ were dissolved in the solution A‴, i.e., $\{Cu(Ac)_2{\cdot}H_2O(s)\}$ + solutionA‴ = solution A″. The results obtained from five dissolution experiments are listed in Table 2.

About 0.05 g of KAc(s) was dissolved in the solution A″, then {KAc(s)} + solution A″ = solution A′. The results obtained from five dissolution experiments are listed in Table 2.

The dilution enthalpy of $H_2O(l)$ as one of the reactants in reaction (1) in solution A′ was within the range of experimental error and may be omitted because the amount of $H_2O(l)$ was very small according to the stoichiometric number of $H_2O(l)$ in reaction (1).

About 0.06 g HAc(l) was dissolved in 100 cm^3 of 5% (v/v) dilute aquaammonia at 298.15 K. Because of the volatilization of acetic acid, when the liquid was weighed, the room temperature must be controlled at 290–291 K to reduce the rate of volatiliza-

Table 2
Dissolution enthalpies of reactants and products of the reaction (1) in the selected solvents at 298.15 K[a].

System	No.	$m_{C_6H_5NO_2}$ (g)	$\Delta E_s/\Delta E_e$	t_e (s)	Q_s (J)	$\Delta_s H_m^o$(kJ mo1^{-1})
Dipicolinic acid (DPA) + s → A‴	1	0.08364	0.99679	64.468	−31.18	−62.36
	2	0.08350	1.00306	64.359	−31.32	−62.70
	3	0.08388	0.78783	81.437	−31.13	−62.03
	4	0.08349	0.99615	64.906	−31.37	−62.80
	5	0.08342	0.99349	64.577	−31.13	−62.37
	Avg $\Delta_s H^\theta_{m,1} = -(62.45 \pm 0.14)$ kJ mo1^{-1}					
$Cu(Ac)_2$ H_2O (s)+ A‴ → A″	1	0.05074	0.79319	50.953	−19.67	−77.45
	2	0.05000	0.87508	45.609	−19.43	−77.71
	3	0.05080	0.71664	55.312	−19.30	−77.18
	4	0.05059	0.87197	45.390	−19.27	−77.06
	5	0.05080	0.87051	45.827	−19.42	−77.67
	Avg $\Delta_s H^\theta_{m,2} = -(77.42 \pm 0.13)$ kJ mo1^{-1}					
KAc (s) + A″ → A′	1	0.04976	0.2806	20.094	−2.74	−5.41
	2	0.05038	0.3267	17.125	−2.72	−5.30
	3	0.05084	0.3669	15.781	−2.82	−5.44
	4	0.04912	0.3534	15.359	−2.64	−5.28
	5	0.04937	0.3715	15.844	−2.87	−5.70
	Avg $\Delta_s H^\theta_{m,3} = -(5.43 \pm 0.07)$ kJ mo1^{-1}					
HAc (aq) + s → B′	1	0.06058	0.8630	105.078	−44.14	−44.14
	2	0.06060	0.9192	100.313	−44.89	−44.89
	3	0.06093	0.9187	100.359	−44.88	−44.88
	4	0.06020	0.9044	100.422	−44.21	−44.21
	5	0.06010	0.8682	105.203	−44.46	−44.46
	Avg $\Delta_s H^\theta_{m,4} = -(44.52 \pm 0.16)$ kJ mo1^{-1}					
$K_2[Cu(DPA)_2]{\cdot}7H_2O$ (s) + B′ → B	1	0.14911	0.0718	18.562	−0.66	−2.63
	2	0.14888	0.0809	13.609	−0.54	−2.15
	3	0.14985	0.2443	4.828	−0.57	−2.30
	4	0.14933	0.3248	4.016	−0.64	−2.54
	5	0.14896	0.3367	4.546	−0.75	−2.99
	Avg $\Delta_s H^\theta_{m,5} = -(2.52 \pm 0.15)$ kJ mo1^{-1}					

[a] m – mass of sample; t_e – heating period of electrical calibration; Q_s – heat effect during the sample dissolution; ΔE_s – the voltage change during the sample dissolution; ΔE_e – the voltage change during the electrical calibration; $\Delta_s H^\theta_m = Q_s/n = (\Delta E_s/\Delta E_e)I^2Rt(M/m)$, where R is the electro-resistance (R = 1216.9 Ω at T = 298.15 K), I is the current (I = 20.015 mA), and M is the molar mass of the sample. The purities for the samples involved in the calorimetric experiments are above 0.995 mass fraction.

Table 3
Dissolution enthalpies of reactants and products of the reaction (2) in the selected solvents at 298.15 K[a].

System	No.	$m_{C_6H_5NO_2}$ (g)	$\Delta E_s/\Delta E_e$	t_e (s)	Q_s (J)	$\Delta_s H_m^o$ (kJ mol^{-1})
Dipicolinic acid $(H_2DPA) + s \rightarrow A'''$	1	0.08364	0.99679	64.468	−31.18	−62.36
	2	0.08350	1.00306	64.359	−31.32	−62.70
	3	0.08388	0.78783	81.437	−31.13	−62.03
	4	0.08349	0.99615	64.906	−31.37	−62.80
	5	0.08342	0.99349	64.577	−31.13	−62.37
	Avg $\Delta_s H^{\theta}_{m,1} = -(62.45 \pm 0.1)$ kJ mo1^{-1}					
$Ni(Ac)_2 \cdot 4H_2O$ $(s) + A''' \rightarrow A''$	1	0.06210	0.41921	27.015	−5.50	−22.02
	2	0.06262	1.02575	11.250	−5.60	−22.25
	3	0.06255	1.02573	11.608	−5.78	−22.99
	4	0.06255	0.98578	11.812	−5.65	−22.48
	5	0.06221	1.0331	11.407	−5.72	−22.88
	Avg $\Delta_s H^{\theta}_{m,2} = -(22.52 \pm 0.18)$ kJ mo1^{-1}					
KAc $(s) + A'' \rightarrow A'$	1	0.05076	0.21635	26.953	−2.84	−5.49
	2	0.04942	0.28012	20.469	−2.78	−5.58
	3	0.04925	0.35618	16.828	−2.92	−5.83
	4	0.04978	0.32335	16.250	−2.56	−5.04
	5	0.04981	0.34089	16.265	−2.70	−5.32
	Avg $\Delta_s H^{\theta}_{m,3} = -(5.45 \pm 0.13)$ kJ mo1^{-1}					
HAc $(aq) + s \rightarrow B'$	1	0.06058	0.8630	105.078	−44.1404	−44.1404
	2	0.06060	0.9192	100.313	−44.8851	−44.8851
	3	0.06093	0.9187	100.359	−44.8792	−44.8792
	4	0.06020	0.9044	100.422	−44.2101	−44.2101
	5	0.06010	0.8682	105.203	−44.4579	−44.4579
	Avg $\Delta_s H^{\theta}_{m,4} = -(44.52 \pm 0.16)$ kJ mo1^{-1}					
$K_2[Ni(DPA)_2]\ 7H_2O$ $(s) + B' \rightarrow B$	1	0.14736	0.13602	17.749	−1.18	−4.74
	2	0.14863	0.19570	12.765	−1.22	−4.86
	3	0.14732	0.17422	12.655	−1.07	−4.33
	4	0.14776	0.19530	12.421	−1.18	−4.74
	5	0.14836	0.17643	12.233	−1.05	−4.20
	Avg $\Delta_s H^{\theta}_{m,5} = -(4.58 \pm 0.13)$ kJ mo1^{-1}					

[a] m – mass of sample; t_e – heating period of electrical calibration; Q_s – Heat effect during the sample dissolution; ΔE_s – The voltage change during the sample dissolution; ΔE_e – The voltage change during the electrical calibration; $\Delta_s H^{\theta}_m = Q_s/n = (\Delta E_s/\Delta E_e) \cdot I^2 Rt(M/m)$, where R is the electro-resistance ($R = 1216.9\ \Omega$ at $T = 298.15$ K), I is the current ($I = 20.015$ mA), and M is the molar mass of the sample. The purities for the samples involved in the calorimetric experiments are above 0.995 mass fraction.

tion. The sample cell in which acetic acid was admitted should be covered with a plug made of polytetrafluoroethylene, then $\{HAc(aq)\}$ + "s" = solution B″. The results obtained from five dissolution experiments are listed in Table 2.

The dissolution enthalpy of $K_2[Cu(DPA)_2]{\cdot}7H_2O(s)$ in solution B′ was measured under the same condition as the above, $\{K_2[Cu(DPA)_2]{\cdot}7H_2O(s)\}$ + solution B′ = solution B. The results obtained from five dissolution experiments are listed in Table 2.

The enthalpy change of the reaction (1) can be calculated in accordance with a thermochemical cycle and the experimental results as follows:

$$\begin{aligned}
&\Delta_r H_{m,1}(\{K_2[Cu(DPA)_2] \cdot 7H_2O(s)\}) = \sum \Delta_s H^o_m(\text{reactants}) \\
&- \sum \Delta_s H^o_m(\text{products}) = 2 \times \Delta H_1 + \Delta H_{2,1} + 2 \times \Delta H_{3,1} + 6 \times \Delta H_4 \\
&- 4 \times \Delta H_5 - \Delta H_{6,1} = 2 \times [-(62.45 \pm 0.14)] + (-77.42 \pm 0.13) \\
&+ 2 \times [-(5.43 \pm 0.07) - 4 \times [(-44.52 \pm 0.16)] - (-2.52 \pm 0.15) \\
&= -(32.58 \pm 0.74)\,\text{kJ mol}^{-1}
\end{aligned}$$

The enthalpy change of reaction (2) can be determined as the above method and all the experimental data are listed in Table 3.

$$\begin{aligned}
&\Delta_r H_{m,2}(\{K_2[Ni(DPA)_2] \cdot 7H_2O(s)\}) = \sum \Delta_s H^o_m(\text{reactants}) \\
&- \sum \Delta_s H^o_m(\text{products}) = 2 \times \Delta H_1 + \Delta H_{2,2} + 2 \times \Delta H_{3,2} + 3 \times \Delta H_4 \\
&- 4 \times \Delta H_5 - \Delta H_{6,2} = 2 \times [-(62.45 \pm 0.14)] + [-(22.52 \pm 0.18)] \\
&+ 2 \times [-(5.45 \pm 0.13)] - 4 \times [-(44.52 \pm 0.16)] - [-(4.58 \pm 0.13)] \\
&= -(24.34 \pm 0.78)\,\text{kJ mol}^{-1}
\end{aligned}$$

3.3. *Standard molar enthalpy of formation of $K_2[M(DPA)_2]{\cdot}7H_2O(s)$ (M = Cu and Ni)*

Two reaction schemes used to derive the standard molar enthalpy of formation of the two complexes are given in Tables 4 and 5. The experimental values of the dissolution enthalpies of the reactants and products in reactions (1) and (2) were combined with some auxiliary thermodynamic data of $\Delta_f H^o_m(C_7H_5NO_4, s) = -(745.1 \pm 2.2)$ kJ mo1^{-1} [6], $\Delta_f H^o_m(Cu(Ac)_2 \cdot H_2O,\ s) = -1193.70$ kJ mo1^{-1} [7], $\Delta_f H^o_m(Ni(Ac)_2 \cdot 4H_2O,\ s) = -2168.2 \pm 1.0$ kJ mo1^{-1} [8], $\Delta_f H^0_m$ (KAc, s) = -725.15 kJ mo1^{-1} [9], $\Delta_f H^o_m(H_2O, l) = -(285.83 \pm 0.04)$ kJ mol^{-1} [10], and $\Delta_f H^o_m(HAc, 1) = -(483.52 \pm 0.36)$ kJ mo1^{-1} [11] to derive the standard molar enthalpies of formation of $K_2[M(DPA)_2] \cdot 7H_2O(s)$(M = Cu and Ni).

$$\begin{aligned}
&\Delta_f H^o_m\{K_2[Cu(DPA)_2] \cdot 7H_2O(s)\} = \Delta H_{12,1} = (2 \times \Delta H_1 + \Delta H_{2,1} \\
&+ 2 \times \Delta H_{3,1} + 6 \times \Delta H_4 - 4 \times \Delta H_5 - \Delta H_{6,1}\ ) + [(2 \times \Delta H_7 \\
&+ \Delta H_{8,1} + 2 \times \Delta H_9 + 6 \times \Delta H_{10}) - 4 \times \Delta H_{11}] \\
&= 2 \times [-(62.45 \pm 0.14)] + [-(77.42 \pm 0.13)] \\
&+ 2 \times [-(5.43 \pm 0.07)] + 6 \times 0 - 4 \times [-(44.52 \pm 0.16)] \\
&- [-(2.52 \pm 0.15)] + \{2 \times [-(745.1 \pm 2.2) + (-1193.70) \\
&+ 2 \times (-725.15) + 6 \times [-(285.83 \pm 0.04) - 4 \times [-(483.52 \pm 0.36)]\} \\
&= -(3947.7 \pm 4.7)\,\text{kJ mol}^{-1}
\end{aligned}$$

Table 4
Reaction scheme used to determine the standard molar formation enthalpy of the compound $K_2[Cu(DPA)_2]{\cdot}7H_2O$ at 298.15 K.

No.	Reaction system	$\Delta_f H_m^o$ or $(\Delta_s H_m^o \pm \sigma_a)^a$ (kJ mol^{-1})
1	$H_2DPA(s) + s = A'''$	$-(62.45 \pm 0.14)$, ΔH_1
2	$Cu(Ac)_2{\cdot}H_2O(s) + A''' = A''$	$-(77.42 \pm 0.13)$, $\Delta H_{2,1}$
3	$KAc(s) + A'' = A'$	$-(5.43 \pm 0.07)$, $\Delta H_{3,1}$
4	$H_2O(l) + A' = A$	0, ΔH_4
5	$HAc(aq) + s = B'$	$-(44.52 \pm 0.16)$, ΔH_5
4	$K_2[Cu(DPC)_2]{\cdot}7H_2O(s) + B' = B$	$-(2.52 \pm 0.15)$, $\Delta H_{6,1}$
5	$7C(s) + 5/2H_2(g) + 1/2\,N_2(g) + 2O_2(g) = H_2DPA\,(s)$	$-(745.1 \pm 2.2)$, ΔH_7
6	$4C(s) + 4H_2(g) + 5/2O_2(g) + Cu(s) = Cu(Ac)_2\,H_2O(s)$	-1193.70, $\Delta H_{8,1}$
7	$K(s) + 2C(s) + O_2(g) + 3/2H_2(g) = KAc(s)$	-725.15, ΔH_9
8	$H_2(g) + 1/2O_2(g) = H_2O(l)$	$-(285.83 \pm 0.04)$, ΔH_{10}
9	$2C(s) + 2H_2(g) + O_2(g) = CH_3COOH(l)$	$-(483.52 \pm 0.36)$, ΔH_{11}
10	$14C(s) + 7H_2(g) + 11/2O_2(g) + Cu(s) = K_2[Cu(DPA)_2]{\cdot}7H_2O(s)$	$-(3947.7 \pm 4.7)$, $\Delta H_{12,1}$

[a] $\sigma_a = \sqrt{\sum_{i=1}^{5}(x_i - \bar{x})^2/(n(n-1))}$ in which n is the experimental number of experiments ($n = 5$); x_i, a single value in a set of dissolution measurements $\bar{x}$ the mean value of a set of measurement results.

Table 5
Reaction scheme used to determine the standard molar formation enthalpy of the compound $K_2[Ni(DPA)_2]{\cdot}7H_2O$ at 298.15 K.

No.	Reaction system	$\Delta_f H_m^o$ or $(\Delta_s H_m^o \pm \sigma_a)^a$ (kJ mol^{-1})
1	$H_2DPA\,(s) + s = A'''$	$-(62.45 \pm 0.14)$, ΔH_1
2	$Ni(Ac)_2{\cdot}4H_2O(s) + A''' = A''$	$-(22.52 \pm 0.18)$, $\Delta H_{2,2}$
3	$KAc(s) + A'' = A'$	$-(5.45 \pm 0.13)$, $\Delta H_{3,2}$
4	$H_2O(l) + A' = A$	0, ΔH_4
5	$HAc(aq) + s = B'$	$-(44.52 \pm 0.16)$, ΔH_5
4	$K_2[Ni(DPC)_2]{\cdot}7H_2O(s) + B' = B$	$-(4.58 \pm 0.13)$, $\Delta H_{6,2}$
5	$7C(s) + 5/2H_2(g) + 1/2\,N_2(g) + 2O_2(g) = H_2DPA\,(s)$	$-(745.1 \pm 2.2)$, ΔH_7
6	$4C(s) + 7H_2(g) + 4O_2(g) + Ni(s) = Ni(Ac)_2\,4H_2O(s)$	$-(2168.2 \pm 1.0)$, $\Delta H_{8,2}$
7	$K(s) + 2C(s) + O_2(g) + 3/2H_2(g) = KAc(s)$	-725.15, ΔH_9
8	$H_2(g) + 1/2O_2(g) = H_2O(l)$	$-(285.83 \pm 0.04)$, ΔH_{10}
9	$2C(s) + 2H_2(g) + O_2(g) = CH_3COOH(l)$	$-(483.52 \pm 0.36)$, ΔH_{11}
10	$14C(s) + 7H_2(g) + 11/2O_2(g) + Ni(s) = K_2[Ni(DPA)_2]{\cdot}7H_2O(s)$	$-(4007.8 \pm 4.7)$, $\Delta H_{12,2}$

[a] $\sigma_a = \sqrt{\sum_{i=1}^{5}(x_i - \bar{x})^2/(n(n-1))}$ in which n is the experimental numbers of experiments ($n = 5$); x_i, a single value in a set of dissolution measurements $\bar{x}$ the mean value of a set of measurement results.

$$\begin{aligned}
\Delta_f H_m^o\{K_2[Ni(DPA)_2]\cdot 7H_2O(s)\} &= \Delta H_{12,2} = (2\times\Delta H_1 + \Delta H_{2,2} \\
&+2\times\Delta H_{3,2} + 3\times\Delta H_4 - 4\times\Delta H_5 - \Delta H_{6,2}) + [(2\times\Delta H_7 + \Delta H_{8,2} \\
&+2\times\Delta H_9 + 3\times\Delta H_{10}) - 4\times\Delta H_{11}] \\
&= 2\times[-(62.45\pm0.14)] + [-(22.52\pm0.18)] \\
&+2\times[-(5.45\pm0.13)] + 3\times 0 - 4\times[-(44.52\pm0.16)] \\
&-[-(4.58\pm0.13)] + \{2\times[-(745.1\pm2.2)] + [-(2168.2\pm1.0)] \\
&+2\times(-725.15) + 3\times[-(285.83\pm0.04) - 4\times[-(483.52\pm0.36)]\} \\
&= -(4007.8\pm4.7)\,\text{kJ mol}^{-1}
\end{aligned}$$

in which ΔH_1 to ΔH_{11} are the enthalpy changes of the reactions corresponding to the number of the reactions in Tables 4 and 5.

The results of UV/vis spectroscopy and refrangibility [12,13] (refractive indices) are two kinds of important information useful for detecting the differences in the structure and composition between two kinds of solutions. In this article, all of the reactants and products of the two reactions can be easily dissolved in the selected solvent. The measured values of the refractive indexes of solution A and solution B are closed to each other. The results of UV/vis spectrophotometry are shown in Figs. 3 and 4. UV/vis spectra and the data of the refractive indices of solution A agree with those of solution B, no difference in the structure and chemical composition existed between the two solutions. These results have demonstrated that solution A and solution B were the same, the designed Hess' thermochemical cycles were reasonable and reliable and can be used to derive the standard molar enthalpies of formation of $K_2[M(DPA)_2]{\cdot}7H_2O(s)$ (M = Cu and Ni).

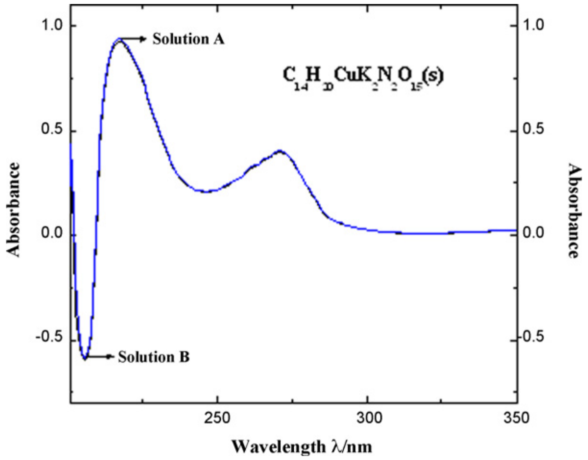

Fig. 3. UV/vis spectra of solution A and solution B (diluted to 1:21) for reaction (1).

3.4. Comparison of the standard molar enthalpies of formation of *$K_2[M(DPA)_2]{\cdot}7H_2O(s)$ (M = Cu and Ni)*

$K_2[Cu(DPA)_2]{\cdot}7H_2O(s)$ and $K_2[Ni(DPA)_2]{\cdot}7H_2O(s)$ are isostructural. The standard molar enthalpies of formation of

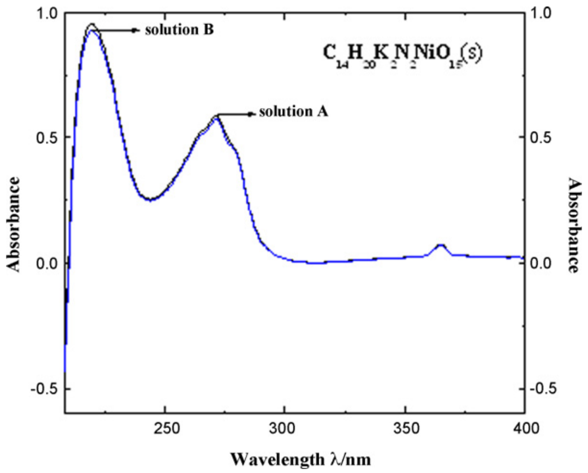

Fig. 4. UV/vis spectra of solution A and solution B (diluted to 1:21) for reaction (2).

$K_2[M(DPA)_2]{\cdot}7H_2O(s)$ (M = Cu and Ni) were determined to be $-(3947.7 \pm 4.7)$ kJ mol^{-1} and $-(4007.8 \pm 4.7)$ kJ mol^{-1}, respectively. By comparing the bond length data of the two complexes, on the one hand, it can be seen that certain differences are existed between the same types of atoms. Essentially speaking, the standard molar enthalpy of formation of the compounds can be used to compare the relative stability of the same type of the compounds. The more negative the standard molar enthalpy of formation of the compound, the more stable the compound. It can be concluded from the results of the experiments that the molar enthalpy of formation of the complex is not only related to metal atomic radius, but also to the bond length between the atoms. On the other hand, the small enthalpy difference of about 60 kJ mol^{-1} between the two isostructural compounds is ascribed to the enthalpy difference between the two acetates when subtracting the enthalpy contribution of the three waters of crystallization. That is to say, the expected similarity in the enthalpies reported is based on the isostructural nature of the complexes and the similarity of Cu and Ni.

4. Conclusions

This paper reports the crystal structures of $K_2[M(DPA)_2]{\cdot}7H_2O(s)$ (M = Cu and Ni) and dissolution enthalpies of the reactants and products of the two designed reactions by isoperibol solution-reaction calorimetry. Additionally, the standard molar enthalpies of formation of $K_2[M(DPA)_2]{\cdot}7H_2O(s)$ (M = Cu and Ni) were derived from these experimental results.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2011.02.008.

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