Low-Temperature Heat Capacities and Thermodynamic Properties of Triaquabenzoatocalcium Monobenzoate $[Ca(Ben)(H_2O)_3](Ben)(s)$ (Ben = Benzoate)

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Triaquabenzoatocalcium monobenzoate $[Ca(Ben)(H_2O)_3](Ben)(s)$ was synthesized by the method of liquid phase reaction. Chemical and element analyses and X-ray crystallography were used to characterize the composition and structure of the complex. The lattice potential energy of the compound was calculated to be $U_{POT} = 426.61\ kJ\cdot mol^{-1}$ on the basis of crystal structure information. Low-temperature heat capacities over the temperature range from (78 to 360) K were measured by an automated adiabatic calorimeter, and a polynomial equation was fitted by the least-squares method. On the basis of the fitted polynomial, the smoothed heat capacities and thermodynamic functions of the compound relative to the standard reference temperature 298.15 K were calculated at intervals of 5 K. The thermal decomposition of the complex was studied using TG and DSC analyses. In accordance with Hess's law, a reasonable thermochemical cycle was designed based on the preparation reaction of the compound. The standard molar enthalpies of dissolution for the reactants and product of the reaction in the selected solvent were measured by an isoperibol solution-reaction calorimeter. The enthalpy change of the liquid phase reaction was calculated to be $\Delta_r H_m^o = -(46.68 \pm 0.40)\ kJ\cdot mol^{-1}$, and the standard molar enthalpy of formation of the complex was determined to be $\Delta_f H_m^o[Ca(Ben)(H_2O)_3](Ben),s = -(2088.2 \pm 1.1)\ kJ\cdot mol^{-1}$ by means of the enthalpy change of the reaction and other auxiliary thermodynamic quantities.

Introduction

It is well-known that calcium is an essential element in the human body, which mainly exists in the body's bones and teeth. It has important physiological functions and nutritional values and can maintain acid−base equilibrium in the human body. Calcium[1] is capable of participating in the process of blood coagulation, maintaining the normal excitability of muscle and nerve cells, and adjusting the permeability of cells and capillary vessels. A shortage of calcium may result in many kinds of diseases, including osteoporosis, nephrolith, sugar diabetes, and cardiovascular diseases and so on. Benzoic acid has prominent physiological and chemical activity as a fine chemical, medical intermediate and food additive in the fields of medicine, cosmetics, and foods, and can be used to synthesize a series of important products. In medicine, benzoic acid, which is a constituent of Whitfield's Ointment used for the treatment of fungal skin diseases,[2] can greatly increase the solubility of the medicine in body fluids and obviously enhance the absorption ratio of drugs in the human body.[3] The compounds of benzoic acid with many metal ions are used as food preservatives and antimicrobial agents in many foods from soup to cereals.

For the compounds of calcium with the benzoate anion, several compounds[4−6] such as $[Ca(Ben)_2]\cdot 3H_2O$, $[Ca(Ben)_2](Ben)_{0.5}\cdot 2H_2O$, $[Ca(Ben)_2]$, and $[Ca(Ben)(H_2O)_3](Ben)$ have been reported. Senkovska et al.[6] have synthesized the complex $[Ca(Ben)(H_2O)_3](Ben)$ by using $CaCl_2$ and potassium benzoate as the reactants and measured the crystal structure of the compound. However, the lattice energy and thermodynamic properties of the compound have not been investigated. Lattice potential energy[7,8] is used to determine the bonding ability of molecules or ions in the crystal structure and reflects many physicochemical properties of the substance. Heat capacity and standard molar enthalpy of formation of a substance are some of the most fundamental thermodynamic properties and are closely related to other physical, biological, physiological, and chemical properties.[9,10] The standard molar enthalpy of formation of a substance is one of the important datum required when calculating enthalpy changes, equilibrium constants, and theoretical yields of reactions in which the substance is involved. In the present work, $[Ca(Ben)(H_2O)_3](Ben)(s)$ was synthesized using different reactants in comparison with the literature.[6] The crystal structure was analyzed by X-ray crystallography, and the TG and DSC techniques were used to study the process of dehydration. The lattice energy was calculated according to the density and molar mass obtained from crystallographic data. The heat capacity and standard molar enthalpy of formation of the title compound were also studied using a precision automatic adiabatic calorimeter and an isoperibol solution-reaction calorimeter, respectively.

Experimental Section

Synthesis and Characterization of $[Ca(Ben)(H_2O)_3](Ben)(s)$. The complex was synthesized according to the method of liquid phase synthesis, in which benzoic acid and calcium hydroxide (of analytical grade) were chosen as the reactants and accurately weighed at the molar ratio of

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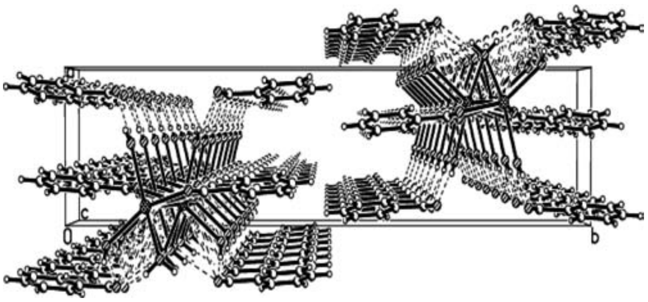

Figure 1. Packing structure of the title compound $[Ca(Ben)(H_2O)_3](Ben)(s)$ in the unit cell.

Table 1. Crystal Data and Structure Refinement for the Title Compound $[Ca(Ben)(H_2O)_3](Ben)(s)$

crystallographic data	structure refinement
empirical formula	$Ca(C_7H_5O_2)(H_2O)_3$, $C_7H_5O_2$
formula weight	336.35
temperature	298(2) K
wavelength	0.71073 Å
crystal system	monoclinic
space group	*P*2(1)/c
unit cell dimensions	$a = 7.2906(8)$ Å, $b = 32.232(3)$ Å, $c = 6.5348(6)$ Å
volume	1535.2(3) Å
Z	4
calculated density	$1.455\ Mg\cdot m^{-3}$
absorption coefficient	$0.440\ mm^{-1}$
F(000)	704
crystal size	0.41 × 0.22 × 0.14 mm
theta range for data collection	1.26 to 25.01°
limiting indices	$-7 \le h \le 8$, $-38 \le k \le 32$, $-7 \le l \le 7$
reflections collected/unique	7649/2698 [*R*(int) = 0.0260]
completeness to theta = 25.01	99.6 %
refinement method	full-matrix least-squares on F^2
data/restraints/parameters	2698/0/199
goodness-of-fit on F^2	1.177
final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0406$, $wR_2 = 0.0911$
R indices (all data)	$R_1 = 0.0496$, $wR_2 = 0.0950$
largest diff. peak and hole	(0.249 and −0.365) $e\cdot Å^{-3}$

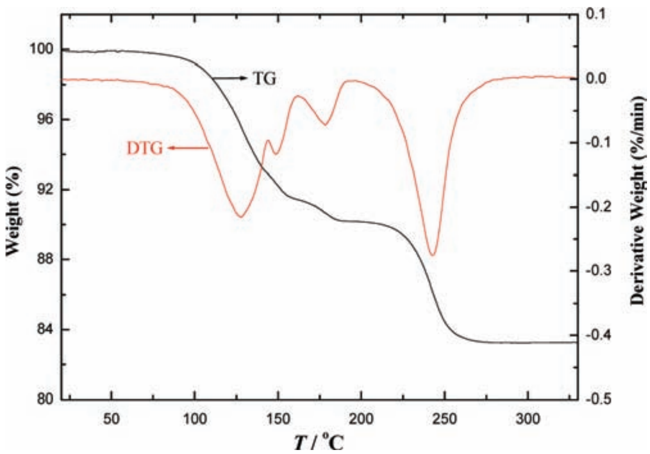

Figure 2. TG−DTG curves of the compound $[Ca(Ben)(H_2O)_3](Ben)(s)$.

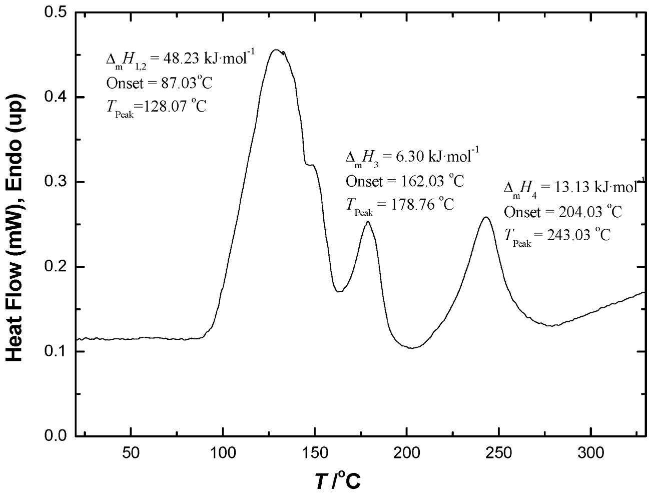

Figure 3. DSC curve of the title compound $[Ca(Ben)(H_2O)_3](Ben)(s)$.

$n(HBen):n(Ca(OH)_2) = 2:1$. First, the right amount of benzoic acid was added into a beaker with double distilled water. When the solution was boiled, the benzoic acid dissolved. Then the equivalent amount of calcium hydroxide was slowly added into the above solution under sufficient stirring. The mixture was boiled and refluxed for 2 h, whereafter the liquid mixture was condensed by boiling off some of the water until a crystal membrane emerged from the solution surface. The final solution was naturally cooled to room temperature and filtered, and a white crystal was obtained. Then, the product was recrystallized three times with double distilled water. The final product was a colorless needle-shaped crystal. The theoretical contents of Ca, C, H, and O in the compound have been calculated to be 11.92 %, 49.99 %, 4.79 %, and 33.30 %, respectively. Chemical and element analyses (model: PE-2400, Perkin-Elmer, USA) have shown that the contents of Ca, C, and H in the compound were measured to be 11.89 %, 49.98 %, and 4.81 %, respectively. This showed that the purity of the sample prepared was higher than 0.9950 in mass fraction.

A single crystal suitable for X-ray analysis was mounted on a fiber. All diffraction data for the compound were collected on a Bruker Smart-1000 CCD area-detector diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 298(2) K using the program SMART and processed by SAINT-plus.[11] Absorption corrections were applied by SADABS.

X-ray crystallography shows that the title compound has the same structure as reported in the literature.[6] The packing structure of triaquabenzoatocalcium monobenzoate $[Ca(Ben)(H_2O)_3](Ben)(s)$ is plotted in Figure 1, and the crystal structure information is listed in Table 1. The benzoate entities participate in coordination action as a bridging ligand between three Ca atoms. The isolated benzoate anion is not linked to the chain by covalent bonds but by strong hydrogen bonds between the carboxyl group and water molecules. In addition, $\pi-\pi$ interactions exist in neighboring phenyl groups. The combination of these hydrogen bonds, $\pi-\pi$ stacking interactions, and Ca−O bonds leads to the formation of a two-dimensional network in the title compound.

The TG−DTG technique was applied to determine the stability of the compound. It can be seen from the TG−DTG curves shown in Figure 2 that four mass-loss processes take place with an increase of temperature. The first mass-loss took place over the temperature range of (87 to 144) °C (the maximum differential mass-loss temperature in the DTG was at 128 °C), and the actual mass-loss percentage was 8.07 %, which is in agreement with the theoretical percent content (8.03 %) of $1.5H_2O$ in the compound. The second mass-loss process happened over the temperature region of (144 to 162) °C (the maximum differential mass-loss temperature in the DTG was at 149 °C), and the actual mass-loss percentage was 0.53 %, which agrees with the theoretical mass-loss (0.54

Table 2. Experimental Molar Heat Capacities of Triaquabenzoatocalcium Monobenzoate $[Ca(Ben)(H_2O)_3](Ben)(s)$ ($M_m = 336.35\ g \cdot mol^{-1}$)

T/K	$C_{p,m}$/$J \cdot K^{-1} \cdot mol^{-1}$	T/K	$C_{p,m}$/$J \cdot K^{-1} \cdot mol^{-1}$	T/K	$C_{p,m}$/$J \cdot K^{-1} \cdot mol^{-1}$
78.800	125.84	165.17	234.25	266.93	361.24
80.620	127.89	168.12	237.66	269.65	364.31
83.350	131.81	171.08	241.70	272.63	367.15
86.010	135.91	174.06	244.96	275.61	370.66
88.590	139.74	177.08	249.12	278.59	374.16
91.092	143.36	180.06	252.85	281.71	377.23
93.580	146.64	184.08	257.01	284.82	380.07
95.954	149.63	188.23	262.04	287.80	383.58
98.306	152.89	191.21	266.42	290.78	387.08
100.66	156.65	193.93	269.05	293.63	390.58
102.85	158.91	197.04	272.77	296.49	393.65
105.21	162.17	200.03	276.50	299.47	397.59
107.40	165.43	203.01	280.66	302.32	400.66
109.44	167.19	205.99	284.60	305.30	403.94
111.64	169.95	208.95	287.41	308.29	407.88
113.68	172.21	211.86	291.37	311.14	410.73
115.87	174.97	214.81	295.11	314.12	414.01
117.91	177.73	217.92	299.05	316.97	417.08
119.95	180.49	220.80	301.90	319.95	420.15
123.14	184.09	223.78	305.67	322.94	423.65
126.77	188.91	226.73	309.78	325.92	427.37
129.70	192.59	229.72	314.16	328.90	430.00
132.67	195.68	232.70	318.10	331.88	432.85
135.59	200.29	235.68	322.04	334.86	436.35
138.57	203.14	238.79	325.77	337.72	440.29
141.55	206.20	242.55	330.58	340.70	443.14
144.53	210.58	246.18	335.18	343.42	446.64
147.39	214.74	249.16	338.91	346.27	450.15
150.37	217.59	252.15	342.19	349.13	453.43
153.35	221.09	255.00	345.26	352.11	457.15
156.33	224.60	257.98	349.85	354.96	460.22
159.26	227.49	260.96	353.80	357.55	463.72
162.21	230.64	263.94	358.39		

%) of $0.1H_2O$ in the compound. The third mass-loss process took place over the temperature region of (162 to 192) °C (the maximum differential mass-loss temperature in the DTG was at 178 °C), and the mass-loss percentage was 1.09 %, which agrees with the theoretical mass-loss (1.07 %) of $0.2H_2O$. The fourth mass-loss process took place over the temperature region of (203 to 279) °C (the maximum differential mass-loss temperature in the DTG was at 243 °C), and the mass-loss percentage was 6.46 %, which agrees with the theoretical mass-loss (6.43 %) of $1.2H_2O$ in the compound.

A possible mechanism for the thermal decomposition of the compound was derived from the results of the TG−DTG analysis as follows

$$[Ca(Ben)(H_2O)_3](Ben) \xrightarrow[8.07\ \%\ (8.03\ \%)]{87\ -\ 128\ -\ 144\ ℃} [Ca(Ben)(H_2O)_{1.5}] \times$$

$$(Ben) \xrightarrow[0.53\ \%\ (0.54\ \%)]{144\ -\ 149\ -\ 162\ ℃} [Ca(Ben)(H_2O)_{1.4}] \times$$

$$(Ben) \xrightarrow[1.09\ \%\ (1.07\ \%)]{162\ -\ 178\ -\ 192\ ℃} [Ca(Ben)(H_2O)_{1.2}] \times$$

$$(Ben) \xrightarrow[6.46\ \%\ (6.43\ \%)]{203\ -\ 243\ -\ 279\ ℃} [Ca(Ben)](Ben)$$

in which the values of the temperatures above the arrows correspond to the starting, the maximum differential mass-loss, and the ending decomposition temperatures of every mass-loss process, and the values below the arrows are the practical mass-loss percentages of every decomposition process (the values in the brackets were obtained from theoretical calculation based on the chemical formula of the compound).

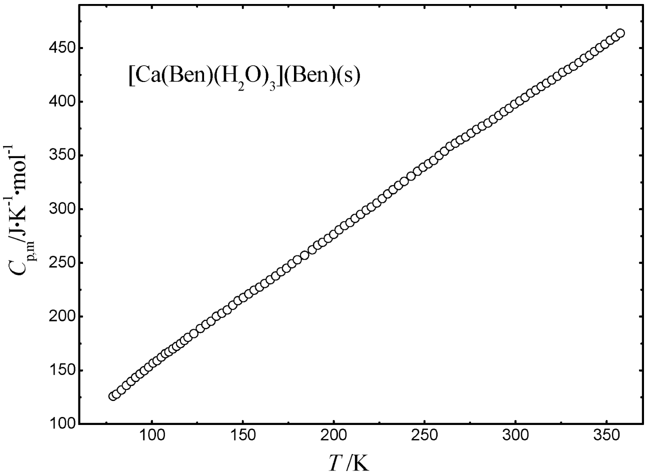

Figure 4. Curve of the experimental molar heat capacities ($C_{p,m}$) vs the temperature (T).

The result of the DSC analysis is plotted in Figure 3. There are four endothermic peaks appearing in the DSC curves. The onset points, peak temperatures (T_{peak}), and molar enthalpies of these endothermic processes were determined to be 87.03 °C, 128.07 °C, and 48.23 $kJ \cdot mol^{-1}$ for the first and second (small) endothermic peaks, which can be wholly regarded as a big endothermic peak, 162.03 °C, 178.76 °C, and 6.30 $kJ \cdot mol^{-1}$ for the third endothermic peak, and 204.03 °C, 243.03 °C, and 13.13 $kJ \cdot mol^{-1}$ for the fourth peak, respectively. The endothermic peaks appearing in the DSC curve correspond with the TG−DTG results of the title compound.

Adiabatic Calorimetry. A precision automatic adiabatic calorimeter was used to measure heat capacities of the compound over the temperature range $78 \le (T/K) \le 400$. The calorimeter was established in the Thermochemistry Laboratory in the College of Chemistry and Chemical Engineering, Liaocheng University, China. The principle and structure of the adiabatic calorimeter are described in detail elsewhere.[12,13] Briefly, the calorimeter mainly comprised a sample cell, a platinum resistance thermometer, an electric heater, inner, middle, and outer adiabatic shields, three sets of six-junction chromel−constantan thermopiles installed between the calorimetric cell and the inner shield, between the inner and middle shields, and between the middle and outer shields, respectively, and a high vacuum can. The miniature platinum resistance thermometer (IPRT No.2, produced by Shanghai Institute of Industrial Automatic Meters, 16 mm in length, 1.6 mm in diameter, and a nominal resistance of 100 Ω) was applied to measure the temperature of the sample. The thermometer was calibrated on the basis of ITS-90 by the Station of Low-Temperature Metrology and Measurements, Academia Sinica. The electrical energy introduced into the sample cell and the equilibrium temperature of the cell after the energy input were automatically recorded by use of a Data Acquisition/Switch Unit (model 34970A, Agilent, USA) and processed online by a computer.

To verify the accuracy of the calorimeter, the heat capacities of a reference standard material (α-Al_2O_3) were measured over the temperature range $78 \le (T/K) \le 400$. The sample mass used was 1.7143 g, which was equivalent to 0.0168 mol based on its molar mass, $M(Al_2O_3) = 101.9613$ $g \cdot mol^{-1}$. Deviations of the experimental results from those of the smoothed curve lie within ± 0.2 %, while the uncertainty is ± 0.3 %, as compared with the values given

Table 3. Smoothed Molar Heat Capacities and Thermodynamic Functions of Triaquabenzoatocalcium Monobenzoate

T	$C_{p,\mathrm{m}}$	$H_T - H_{298.15\ \mathrm{K}}$	$S_T - S_{298.15\ \mathrm{K}}$	$G_T - G_{298.15\ \mathrm{K}}$
K	$\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$	$\mathrm{kJ \cdot mol^{-1}}$	$\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$	$\mathrm{kJ \cdot mol^{-1}}$
80	128.89	−57.604	−309.92	−32.810
85	135.26	−56.944	−301.93	−31.280
90	141.62	−56.251	−294.02	−29.790
95	147.97	−55.527	−286.19	−28.340
100	154.30	−54.772	−278.43	−26.929
105	160.62	−53.984	−270.74	−25.557
110	166.93	−53.166	−263.11	−24.224
115	173.22	−52.315	−255.54	−22.928
120	179.51	−51.433	−248.03	−21.670
125	185.78	−50.520	−240.57	−20.449
130	192.03	−49.576	−233.16	−19.265
135	198.28	−48.600	−225.79	−18.118
140	204.51	−47.593	−218.47	−17.007
145	210.73	−46.555	−211.19	−15.933
150	216.94	−45.485	−203.94	−14.894
155	223.14	−44.385	−196.73	−13.892
160	229.32	−43.254	−189.56	−12.925
165	235.50	−42.092	−182.41	−11.994
170	241.65	−40.899	−175.30	−11.099
175	247.80	−39.675	−168.21	−10.239
180	253.94	−38.421	−161.15	−9.4142
185	260.06	−37.136	−154.11	−8.6250
190	266.17	−35.821	−147.10	−7.8711
195	272.26	−34.474	−140.11	−7.1523
200	278.35	−33.098	−133.15	−6.4687
205	284.42	−31.691	−126.20	−5.8200
210	290.48	−30.254	−119.27	−5.2063
215	296.53	−28.786	−112.37	−4.6274
220	302.57	−27.288	−105.48	−4.0832
225	308.59	−25.761	−98.608	−3.5737
230	314.60	−24.203	−91.756	−3.0987
235	320.60	−22.615	−84.922	−2.6580
240	326.58	−20.997	−78.104	−2.2517
245	332.56	−19.349	−71.303	−1.8795
250	338.52	−17.671	−64.519	−1.5413
255	344.47	−15.964	−57.751	−1.2370
260	350.40	−14.226	−51.000	−0.96650
265	356.33	−12.460	−44.264	−0.72960
270	362.24	−10.663	−37.544	−0.52618
275	368.14	−8.8372	−30.840	−0.35611
280	374.03	−6.9818	−24.152	−0.21927
285	379.90	−5.0970	−17.479	−0.11554
290	385.76	−3.1828	−10.821	−0.044809
295	391.61	−1.2394	−4.1776	−0.0069774
298.15	395.29	0	0	0
300	397.45	0.73329	2.4508	−0.0019673
305	403.27	2.7351	9.0650	−0.029717
310	409.09	4.7660	15.665	−0.090188
315	414.89	6.8260	22.252	−0.18337
320	420.67	8.9149	28.826	−0.30928
325	426.45	11.033	35.387	−0.46796
330	432.21	13.179	41.936	−0.65952
335	437.96	15.355	48.474	−0.88409
340	443.70	17.559	55.003	−1.1419
345	449.43	19.792	61.522	−1.4330
350	455.14	22.053	68.032	−1.7580
355	460.84	24.343	74.536	−2.1170

by the former National Bureau of Standards[14] over the whole temperature range.

Heat capacity measurements were continuously and automatically carried out by means of the standard method of intermittently heating the sample and alternately measuring the temperature. The heating rate and temperature increments were generally controlled at (0.1 to 0.4) $\mathrm{K \cdot min^{-1}}$ and (1 to 3) K. The heating duration was 10 min, and the temperature drift rates of the sample cell measured in an equilibrium period were always kept within (10^{-3} to 10^{-4}) $\mathrm{K \cdot min^{-1}}$ during the acquisition of all heat capacity data. The data of heat capacities and corresponding equilibrium temperature have been corrected for heat exchange of the sample cell with its surroundings.[12] The sample mass used for calorimetric measurements was 3.1287 g, which was equivalent to $9.3019 \cdot 10^{-3}$ mol in terms of its molar mass, $M_\mathrm{m} = 336.35\ \mathrm{g \cdot mol^{-1}}$.

Isoperibol Solution-Reaction Calorimetry. The isoperibol solution-reaction calorimeter consisted primarily of a precision temperature controlling 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. The principle and structure of the calorimeter are described in detail elsewhere.[12,15]

The thermistor was adopted as the sensor for controlling temperature in the thermostatic bath. The input signal of the modified high-precision temperature controller (model: DWT-702, manufactured by Shanghai No. 6 Automated Instrumentation Works), which worked in the PID (proportional-integral-derivative) mode, was not obtained directly from the thermistor sensor but from the signal of the self-made Wheatstone electric bridge used for temperature control. Water was used as the thermostatic medium. During the whole experiment, the water thermostat was automatically maintained at $T = (298.150 \pm 0.001)$ K by regulating an adjustable precision resistor in the Wheatstone bridge. Experiments[15] have demonstrated that the precision of temperature control of this kind of system can reach $\pm 1 \cdot 10^{-3}$ K.

The calorimetric body consisted of the calorimetric chamber, the electric stirrer, the temperature measurement system, and the sampling system. The system for measuring temperature consisted of a Wheatstone electric bridge similar to that of the temperature control system and another thermistor with a large negative temperature coefficient of resistance. The thermistor used as a thermometer was calibrated on the basis of ITS-90 by the station of Low-Temperature Metrology and Measurements, Academia Sinica. A Data Acquisition/Switch Unit (model: 34970A, Agilent, USA) was used to determine the temperature of the solution in the chamber with a precision of 0.1 mK. The unbalanced voltage signal had a linear response to the change of temperature over the temperature range from (295 to 310) K. Measurements[15] indicate that the precision of the temperature measurement system can reach $\pm 1 \cdot 10^{-4}$ K at least, and the time constant of the calorimeter was about 3 s. The system of electric energy calibration consisted of the electric heater and the precision power supply with stepwise constant currents. During each electrical energy calibration, the electrical current through the heater was set at $I = 20.015$ mA, and the resistance of the electrical heater was $R = 1213.09\ \Omega$ at $T = 298.15$ K.

The reliability of the calorimeter was verified previously by measuring the dissolution enthalpy of KCl (calorimetric primary standard) in double distilled water at $T = 298.15$ K. The mean dissolution enthalpy was $(17547 \pm 13)\ \mathrm{J \cdot mol^{-1}}$ for KCl, which compares with corresponding published data, $(17536 \pm 3.4)\ \mathrm{J \cdot mol^{-1}}$.[16]

In all dissolution experiments of the sample, 100 mL of 1.0 $\mathrm{mol \cdot L^{-1}}$ HCl was chosen as the calorimetric solvent for measuring the dissolution enthalpies of the reactants and product at $T = 298.15$ K.

Finally, UV/vis spectroscopy and refractive indexes were used to confirm whether the initial solution was in the same thermodynamic state as that of the reacted solutions.

Results and Discussion

Lattice Potential Energy. Triaquabenzoatocalcium monobenzoate $[\mathrm{Ca(Ben)(H_2O)_3}](\mathrm{Ben})(\mathrm{s})$ can be regarded as a simple salt

Table 4. Dissolution Enthalpies of Reactants and Product of Reaction 6 in the Selected Solvent at $T = 298.15$ K[a]

		avg. $\Delta_sH_m^o$		m		t_e	Q_s	$\Delta_sH_m^o$
system	solvent	($kJ\cdot mol^{-1}$)	no.	g	$\Delta E_s/\Delta E_e$	s	J	$kJ\cdot mol^{-1}$
benzoic acid	1.0 $mol\cdot L^{-1}$ HCl	(29.48 ± 0.17)	1	0.07331	−0.74199	49.359	17.798	29.648
			2	0.07327	−0.92285	40.109	17.988	29.980
			3	0.07317	−0.88231	40.843	17.512	29.228
			4	0.07317	−0.88070	40.609	17.380	29.007
			5	0.07331	−0.90732	40.218	17.733	29.540
calcium hydroxide	solution A′	−(93.02 ± 0.20)	1	0.02243	0.89593	64.375	−28.028	−92.582
			2	0.02242	0.96378	60.312	−28.248	−93.349
			3	0.02253	0.97060	60.344	−28.463	−93.600
			4	0.02238	0.94415	60.969	−27.974	−92.609
			5	0.02244	0.90456	64.062	−28.161	−92.978
triaquabenzoatocalcium monobenzoate	1.0 $mol\cdot L^{-1}$ HCl	(12.62 ± 0.06)	1	0.10091	−0.26583	29.109	3.7604	12.534
			2	0.10095	−0.39705	20.015	3.8620	12.867
			3	0.10103	−0.38425	20.266	3.7843	12.599
			4	0.10101	−0.37261	20.875	3.7800	12.587
			5	0.10095	−0.37589	20.578	3.7590	12.524

[a] m (g), mass of sample; t_e (s), heating period of electrical calibration; $Q_s = -(\Delta E_s/\Delta E_e)\cdot I^2Rt_e$, heat effect during the sample dissolution; ΔE_s (mV), the voltage change during the sample dissolution; ΔE_e (mV), the voltage change during the electrical calibration; $\Delta_sH_m^o = Q_s/n = -(\Delta E_s/\Delta E_e)\cdot I^2Rt_e(M_m/m)$, where R is the electro-resistance ($R = 1213.09\ \Omega$ at $T = 298.15$ K), I is the current ($I = 20.015$ mA), and M_m is the molar mass of the sample.

Table 5. Reaction Scheme Used to Determine the Standard Molar Enthalpy of Formation of Triaquabenzoatocalcium Monobenzoate $[Ca(Ben)(H_2O)_3](Ben)(s)$

			$\Delta_fH_m^o$ or $(\Delta_sH_m^o \pm \sigma_a)$[a]
no.	reactions	formed solution	$kJ\cdot mol^{-1}$[a]
1	$\{HBen(s)\} + $ "S" =	A′	(29.48 ± 0.17), ΔH_1
2	$\{Ca(OH)_2(s)\}$ + solution A′ =	A	−(93.02 ± 0.20), ΔH_2
3	$\{[Ca(Ben)(H_2O)_3](Ben)(s)\} + $ "S" =	B	(12.62 ± 0.06), ΔH_3
4	$7C(s) + 3H_2(g) + O_2(g) = HBen(s)$		−(384.80 ± 0.50), ΔH_4
5	$Ca(s) + H_2(g) + O_2(g) = Ca(OH)_2(s)$		−986.09, ΔH_5
6	$H_2(g) + (1/2)O_2(g) = H_2O(l)$		−(285.83 ± 0.04), ΔH_6
7	$Ca(s) + 14C(s) + 8H_2(g) + (7/2)O_2(g) = [Ca(Ben)(H_2O)_3](Ben)(s)$		−(2088.2 ± 1.1), ΔH_7

[a] The calorimetric solvent "S" is 1.0 $mol\cdot L^{-1}$ HCl, $\sigma_a = [(\sum_{i=1}^{5}(x_i - \bar{x})^2)/(n(n-1))]^{1/2}$ in which n is the experimental number; x_i is a single value in a set of dissolution measurements; and $\bar{x}$ is the mean value of a set of measurement results.

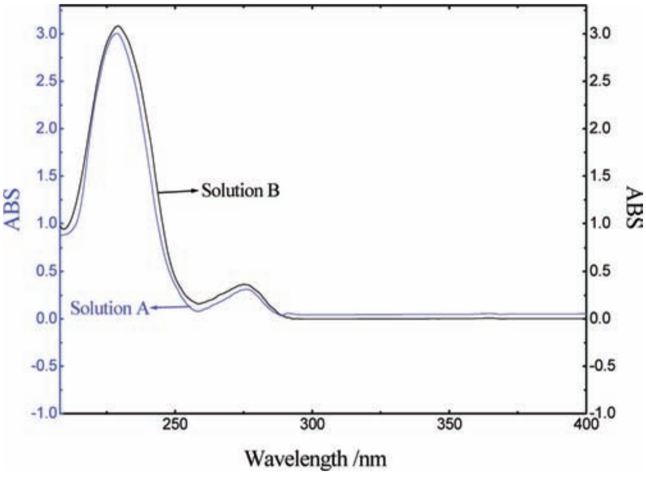

Figure 5. UV/vis spectra of solution A obtained from dissolution of the reactants in the liquid phase reaction and solution B from dissolution of the product (diluted to 1:20).

of the type of MX (1:1), and the lattice potential energy of the complex can be obtained from the formula[7]

$$U_{POT} = \gamma'\left(\frac{\rho}{M_m}\right)^{1/3} + \delta \quad (1)$$

in which the constants of $\gamma' = 1981.2\ kJ\cdot mol^{-1}\cdot cm$ and $\delta = 103.8\ kJ\cdot mol^{-1}$ for MX (1:1) salts.

From the crystal structure information of Table 1, $\rho = 1.455\ g\cdot cm^{-3}$, $M_m = 336.35\ g\cdot mol^{-1}$, and the lattice potential energy of the complex $[Ca(Ben)(H_2O)_3](Ben)(s)$ is calculated as $U_{POT} = 426.61\ kJ\cdot mol^{-1}$.

Low-Temperature Heat Capacities. The initial dehydration temperature of the compound is about 87 °C (360.15 K), as seen from the TG−DTG and DSC analyses. The obtained heat capacities are from (78 to 360) K. The experimental molar heat capacities are listed in Table 2 and plotted in Figure 4, which show that the structure of the complex is stable over the temperature range between $T = 78$ K and $T = 360$ K; i.e., no phase change, association, nor thermal decomposition occurred. The 98 experimental points were fitted by a least-squares method, and a polynomial equation of molar heat capacities ($C_{p,m}$) vs reduced temperature (X), $X = f(T)$, has been obtained

$$C_{p,m}/(J\cdot K^{-1}\cdot mol^{-1}) = A + BX + CX^2 \quad (2)$$

in which $A = 301.360$, $B = 170.094$, $C = -4.922$, and $X = (T - 219)/141$. This equation is valid over the temperature range from (78 to 360) K.

The standard deviations of experimental molar heat capacities from the smoothed heat capacities calculated by the polynomial equation were within ± 0.50 % except for several points around the lower and upper temperature limits. The coefficient of determination for the fitting R^2 equals 0.99986. The uncertainties of the coefficients (A, B, and C) in eq 2 have been determined to be 0.06 %, 0.12 %, and 8.31 %, respectively. Although the deviation of coefficient C is a little large, the influence of the coefficient C on the results of molar heat capacities ($C_{p,m}$) is very small.

Thermodynamic Functions of the Complex. The smoothed molar heat capacities and thermodynamic functions of the sample were calculated based on the fitted polynomial of the heat capacity as a function of the reduced temperature (X) according to the following thermodynamic equations

$$(H_T - H_{298.15}) = \int_{298.15}^{T} C_p\cdot dT \quad (3)$$

$$(S_T - S_{298.15}) = \int_{298.15}^{T} C_p\cdot T^{-1}dT \quad (4)$$

$$(G_T - G_{298.15}) = \int_{298.15}^{T} C_p \cdot \mathrm{d}T - T\int_{298.15}^{T} C_p \cdot T^{-1}\mathrm{d}T \qquad (5)$$

The polynomial fitted values of the molar heat capacities and fundamental thermodynamic functions of the sample relative to the standard reference temperature 298.15 K are tabulated in Table 3 at an interval of 5 K.

Determination of Enthalpy Change for the Liquid Phase Reaction of Ca(OH)₂(s) with Benzoic Acid. The liquid phase reaction of $Ca(OH)_2(s)$ with benzoic acid is shown as follows

$$2\mathrm{HBen(s)} + \mathrm{Ca(OH)_2(s)} + \mathrm{H_2O(l)} \rightarrow [\mathrm{Ca(Ben)(H_2O)_3}](\mathrm{Ben})(\mathrm{s}) \qquad (6)$$

The enthalpy change of reaction 6 can be determined by measuring the enthalpies of dissolution of HBen(s) and $[Ca(Ben)(H_2O)_3](Ben)(s)$ in 1.0 mol·L^{-1} HCl and $Ca(OH)_2(s)$ in 1.0 mol·L^{-1} HCl solution containing certain amounts of the benzoic acid at 298.15 K.

First, benzoic acid and calcium hydroxide must be dried in a vacuum desiccator at 50 °C for several hours. About 0.6 mmol or 0.0733 g of HBen(s) was dissolved in 100 mL of 1.0 mol·L^{-1} HCl at 298.15 K. If "S" = calorimetric solvent, 1.0 mol·L^{-1} HCl, then

$$\{\mathrm{HBen(s)}\} + \text{“S”} = \text{solution A}'$$

According to the $n\{(Ca(OH)_2):(HBen)\} = 1:2$ in reaction 6, about 0.3 mmol or 0.0222 g of $\{Ca(OH)_2,s\}$ was dissolved in solution A′, i.e.

$$\{\mathrm{Ca(OH)_2(s)}\} + \text{solution A}' = \text{solution A}$$

About 0.3 mmol or 0.1009 g of $\{[Ca(Ben)(H_2O)_3](Ben)(s)\}$ was dissolved in 100 mL of 1.0 mol·L^{-1} HCl. The dissolution enthalpy was measured under the same conditions as above

$$\{[\mathrm{Ca(Ben)(H_2O)_3}](\mathrm{Ben})(\mathrm{s})\} + \text{“S”} = \text{solution B}$$

In addition, the dilution enthalpy of reactant $\{H_2O(l)\}$ in reaction 6 is within the experimental error, cannot be measured, and may be omitted.

The measurement results of dissolution enthalpies for the reactants and product of reaction 6 are listed in Table 4.

The enthalpy change of reaction 6 can be calculated in accordance with a thermochemical cycle and the experimental results of the dissolution enthalpy as follows

$$\Delta_r H_m^o = \sum \Delta_s H_{m(\mathrm{Reactants})}^o - \sum \Delta_s H_{m(\mathrm{Products})}^o = (2\Delta_s H_{\mathrm{HBen}}^o + \Delta_s H_{\mathrm{Ca(OH)_2}}^o + \Delta_s H_{\mathrm{H_2O}}^o) - \Delta_s H_{[\mathrm{Ca(Ben)(H_2O)_3}](\mathrm{Ben})}^o = (2\Delta H_1 + \Delta H_2 + 0) - \Delta H_3 = [2 \cdot 29.481 + (-93.024)] - 12.622 = -(46.68 \pm 0.40)\,\mathrm{kJ \cdot mol^{-1}}$$

Standard Molar Enthalpy of Formation of the Title Compound. A reaction scheme used to determine the standard molar enthalpy of formation of $[Ca(Ben)(H_2O)_3](Ben)(s)$ is given in Table 5. The experimental values of the dissolution enthalpies of the reactants and product in the liquid phase reactions 6 were combined with other auxiliary thermodynamic data of $\Delta_f H_m^o(\mathrm{HBen, s}) = -(384.80 \pm 0.50)$ kJ·mol^{-1},[17] $\Delta_f H_m^o[\mathrm{Ca(OH)_2, s}] = -986.09$ kJ·mol^{-1},[18] and $\Delta_f H_m^o(\mathrm{H_2O, l}) = -(285.83 \pm 0.04)$ kJ·mol^{-1},[19] to derive the standard molar enthalpy of formation of the compound

$$\begin{aligned}
\Delta_f H_m^o&[\mathrm{Ca(Ben)(H_2O)_3}](\mathrm{Ben}),\mathrm{s} = \Delta H_7 \\
&= \Delta_r H_m^o + 2\Delta_f H_m^o(\mathrm{HBen,s}) + \Delta_f H_m^o[\mathrm{Ca(OH)_2, s}] + \Delta_f H_m^o(\mathrm{H_2O, l}) \\
&= [(2\Delta H_1 + \Delta H_2) - \Delta H_3] + 2\Delta H_4 + \Delta H_5 + \Delta H_6 \\
&= [2 \cdot 29.481 + (-93.024) - 12.622] + 2 \cdot (-384.80) + (-986.09) + (-285.83) \\
&= -(2088.2 \pm 1.1)\,\mathrm{kJ \cdot mol^{-1}}
\end{aligned}$$

in which $\Delta H_1 \sim \Delta H_7$ were the enthalpy changes of the reactions corresponding to the number of the reactions in Table 5.

In this paper, solution A from the dissolution of reactants in reaction 6 was in a thermodynamically equivalent state to solution B, which was confirmed by UV/vis spectroscopy and the refractive indices of two solutions (A and B). The measured values of the refractive indices were (1.3501 ± 0.0002) for solution A and (1.3503 ± 0.0001) for solution B. The absorbance of the UV/vis spectroscopy is shown in Figure 5. The UV/vis spectrum and the value of the refractive index of solution A obtained agree with those of solution B. These results demonstrate that the chemical components and physicochemical properties of solution A were consistent with those of solution B. As a result, the designed thermochemical cycle was reasonable and reliable and can be used to calculate the standard molar enthalpy of formation of the title compound, triaquabenzoatocalcium monobenzoate.

Conclusions

(1) This paper reports the crystal structure, low temperature heat capacities of the title compound, and the dissolution enthalpies of the reactants and the product of the liquid phase reaction of calcium hydroxide with benzoic acid. Furthermore, the lattice potential energy, thermodynamic functions, and standard molar enthalpy of formation of the compound are also derived from these experimental results.

(2) The reliability of the designed thermochemical cycle has been verified by UV spectroscopy and refractive indexes. It is shown that the cycle is reasonable and can be used to determine standard molar enthalpy of formation of $[Ca(Ben)(H_2O)_3](Ben)(s)$, which is negative with a large absolute value. The results show that the title compound has a lower energy and more stable structure in comparison with the stable substances from which it was made.

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