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LOW TEMPERATURE HEAT CAPACITY OF THE COORDINATION COMPOUND

Nickel(II) nitrate with 4-amine-1,2,4-triazole at temperatures from 11 to 317 K

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Abstract

Low-temperature heat capacity of the coordination compound of nickel(II) nitrate with 4-amine-1,2,4-triazole was measured in the temperature range from 11 to 317 K using a computerized vacuum adiabatic calorimeter. The thermodynamic functions have been derived from the smoothed experimental data over the whole temperature interval covered and at standard conditions. At 298.15 K, the heat capacity is 574.7±1.2 J K^{-1} mol^{-1}, the entropy is 599.2±1.2 J K^{-1} mol^{-1}, the enthalpy is 91070±200 J mol^{-1}, and the reduced Gibbs energy is 293.7±1.2 J K^{-1} mol^{-1}. The results on $C_p(T)$ were compared with those for $Cu(NH_2trz)_3(NO_3)_2{\cdot}0.5H_2O$. It was revealed that the slope of the curve $dC_p/dT\,(T)$ changes essentially for both compounds at 110–120 K. It implies that additional degrees of freedom appear in the heat capacity at these temperatures.

Keywords: heat capacity, nickel complex compounds, thermodynamic functions, triazole derivatives

Introduction

So far there are only a few works published on low-temperature thermodynamic properties of coordination compounds with poly-nitrogen-containing ligands. In 1997, the heat capacity $C_p(T)$ of two complex compounds of Fe(II) and Cu(II) with 4-amino-1,2,4-triazole $C_2H_4N_4$ (further designated as NH_2trz), $Fe(NH_2trz)_3(NO_3)_2$ and $Cu(NH_2trz)_3(NO_3)_2{\cdot}0.5H_2O$, was studied in a wide temperature range [1]. Further research was conducted to study heat capacity of $Fe(NH_2trz)_3Br_2{\cdot}H_2O$ and $Fe(NH_2trz)_3(ClO_4)_2$ [2], yielding the abnormal behavior of $C_p(T)$ for all complexes of iron as result. It was connected to the phase transitions from low-spin to high-spin state (LS→HS). Thermodynamic and structural properties of complex compounds, and also phase transition from low-spin to high-spin state were studied also in the

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papers [3, 4]. However, the nature of the LS→HS phase transition is not clear yet. Thus, for some compounds ($Fe(NH_2trz)_3(ClO_4)_2$) the hysteresis of the transition temperature was not observed whereas for others ($Fe(NH_2trz)_3Br_2$, $Fe(NH_2trz)_3(NO_3)_2$ etc.) the hysteresis is about 20–30 K [1, 2]. This parameter is of great practical importance for stability of memory devices based on coordination compounds. It was suggested that LS→HS phase transition is determined by a cooperative Jahn–Teller dynamic interaction, and hysteresis depends on second coordination sphere of iron ion [5]. Substituting iron-ion with another metal-ion of different electron shell, it is possible to study phonon properties of coordination compounds because the influence of the phase transition will be eliminated. The goal of this research was to study thermodynamic properties of the complex compound of Ni(II) with a composition $Ni(NH_2trz)_3(NO_3)_2{\cdot}H_2O$.

Experimental

A sample of $Ni(NH_2trz)_3(NO_3)_2{\cdot}H_2O$ was synthesized by interaction of ethanol solutions of $Ni(NO_3)_2$ and NH_2trz. A more detailed description of synthesis procedure can be found in the article [6]. The nickel content in the sample was defined through chemical analysis after decomposition of samples in a mixture of concentrated H_2SO_4 and $HClO_4$ (1:2). Standard procedures were used to conduct element analysis for carbon, hydrogen and nitrogen.

The results of analyses are following (mass%): carbon – 16.0±0.3; hydrogen – 2.7±0.3; nitrogen – 43.3±0.3; nickel – 12.9±0.1. The calculated data for $C_6H_{14}N_{14}O_7Ni$: C – 15.9; H – 3.1; N – 43.3 and Ni – 13.0.

The amount of water in the complex was derived from the results of mass loss measurements at heating. The batch of 1.0460 g was maintained at 150°C until constant mass was achieved. The mass loss was 0.0444 g, i.e. 4.24%. It corresponds to one molecule of water in the formula. The formula mass was taken to be 452.98 g mol^{-1}.

Measurements of the heat capacity $C_p(T)$ were carried out in the temperature range from 5.5 to 317 K using a computerized vacuum adiabatic calorimeter with a nickel ampoule, as described earlier [7]. The mass of the specimen was 3.0136 g.

Results and discussion

The measurements were made at routine pressure of $1.3{\cdot}10^3$ Pa of heat exchanging helium in the calorimeter ampoule. In the process the derived heat capacity of the sample was found to be equal to zero in the 10 experiments at temperatures from 5.5 to 11 K, that is heat input into the calorimeter resulted only in heating of the calorimeter ampoule. It was assumed that the observed effect could be due to the total absorption of heat exchanging helium by the sample. To check this assumption, the curve was performed under adiabatic conditions over an interval 6–12 K at a heating rate of 0.1 K min^{-1}. In spite of permanent heat input into the calorimeter, the temperature of the ampoule at 10.85 K decreased down to 10.7 K, which could be, in our opinion, attributed to desorption of helium and to equalizing of the temperature of ampoule with temperature of sample. To eliminate an effect of entire absorption of helium by the sample at low temperatures the calorimetric ampoule was filled with excess amount of gas with pressure of $1.0\cdot10^5$ Pa. After this second filling nonzero values of the heat capacity of the sample were obtained in the temperature range 6–11 K. The correction for the heat capacity of excess gaseous helium was introduced in these experiments, but the values of $C_p(T)$ at $12<T<30$ K were found above the results obtained at the helium pressure of $1.3\cdot10^3$ Pa. The difference was about 2% at 12 K and gradually decreased down to zero as approaching 30 K (top curve in Fig. 1). This difference in the heat capacity values obtained at different pressure of helium, probably can be explained by partial desorption of helium, however it is not possible to prove the fact quantitatively. Therefore the data obtained at the pressure of heat exchanging helium of $1.3\cdot10^3$ Pa were used for calculation of thermodynamic functions. These data are given in Table 1.

Table 1 Experimental values of heat capacity (J K^{-1} mol^{-1}) of $Ni(NH_2trz)_3(NO_3)_2\cdot H_2O$

T/K	C_p	T/K	C_p	T/K	C_p	T/K	C_p
11.54	9.075	49.31	115.3	152.31	318.1	266.42	524.1
11.55	9.280	52.62	124.6	162.12	334.3	270.88	532.9
12.73	11.94	56.38	134.7	172.10	351.2	271.93	533.5
13.12	12.84	59.06	141.7	182.01	368.9	275.79	540.8
14.37	15.79	60.45	144.2	191.82	386.5	277.45	543.2
14.87	17.02	64.19	154.7	199.98	401.2	282.97	551.9
16.78	21.61	69.33	166.0	200.89	403.7	283.21	552.5
18.66	26.41	74.32	178.0	205.90	413.9	288.50	560.2
20.56	31.37	79.15	190.0	206.56	414.8	293.14	567.4
22.42	36.49	81.29	194.9	210.94	423.2	293.61	568.1
24.30	41.71	83.86	200.1	215.22	429.4	294.62	570.7
26.17	47.11	84.76	202.1	215.97	431.1	300.21	578.2
28.00	52.54	90.50	213.8	221.04	440.7	301.09	578.4
30.26	59.30	97.76	228.1	225.88	449.2	304.66	583.5
32.98	66.62	105.14	241.3	236.62	468.3	305.78	585.4
35.65	75.42	113.57	255.8	247.34	488.4	310.67	592.0
38.84	84.87	123.08	271.6	258.03	507.6	311.33	593.7
42.38	95.31	132.72	287.0	260.92	512.6	316.89	600.9
45.90	105.5	142.51	302.5	265.92	521.9		

To calculate thermodynamic functions, the experimental dependence $C_p(T)$ was smoothed using spline functions. The program of calculation provided extrapolation of experimental data from 11 to 0 K according to a cubic function of T. The derived values of heat capacity, entropy, enthalpy and reduced Gibbs energy at some selected temperatures are given in Table 2.

Table 2 Smoothed values of the heat capacity and the thermodynamic functions of $Ni(NH_2trz)_3(NO_3)_2 \cdot H_2O$

T/K	C°_p/J K^{-1} mol^{-1}	$S^\circ_T - S^\circ_0$/J K^{-1} mol^{-1}	$H^\circ_T - H^\circ_0$/J mol^{-1}	Φ°_T/J K^{-1} mol^{-1}
11.54	9.086	3.029	26.22	0.757
15	17.34	6.438	71.83	1.649
20	29.97	13.13	189.6	3.647
25	43.74	21.28	373.5	6.338
30	58.28	30.53	628.3	9.585
35	73.17	40.63	956.8	13.29
40	88.11	51.38	1360	17.37
45	102.8	62.60	1837	21.77
50	117.0	74.17	2387	26.43
60	143.7	97.9	3692	36.36
70	168.5	121.9	5255	46.87
80	191.5	146.0	7056	57.75
90	212.7	169.8	9079	68.88
100	232.0	193.2	11300	80.14
120	266.6	238.6	16300	102.8
140	298.7	282.1	21950	125.3
160	331.2	324.1	28250	147.6
180	365.6	365.1	35210	169.5
200	401.9	405.5	42890	191.0
220	438.8	445.5	51290	212.4
240	475.5	485.3	60440	233.5
260	511.9	524.8	70310	254.3
280	546.4	564.0	80900	275.1
300	577.5	602.8	92140	295.6
316.89	602.7	635.1	102100	312.9
298.15	574.7±1.2	599.2±1.2	91070±200	293.7±1.2

Accuracy of the cited values at the standard temperature 298.15 K was estimated considering the accuracy of measurements of standard substance i.e. benzoic acid [6], and of scatter of experimental points.

The temperature dependence of the heat capacity of $Ni(NH_2trz)_3(NO_3)_2{\cdot}H_2O$ has no well-defined anomalies. The same is true for $Cu(NH_2trz)_3(NO_3)_2{\cdot}0.5H_2O$ [1]. Nevertheless, we found it interesting to compare results for both substances (Fig. 2).

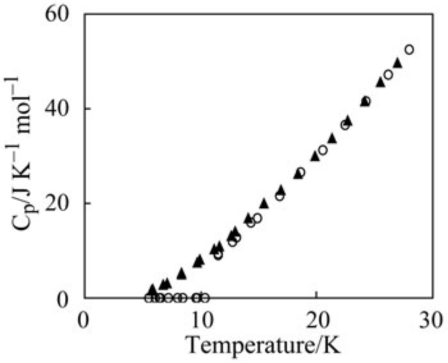

Fig. 1 Molar heat capacity of $Ni(NH_2trz)_3(NO_3)_2{\cdot}H_2O$ at lowest temperatures: circles represent measurements at the pressure of heat exchanging helium of $1.3{\cdot}10^3$ Pa; triangles – at $1.0{\cdot}10^5$ Pa

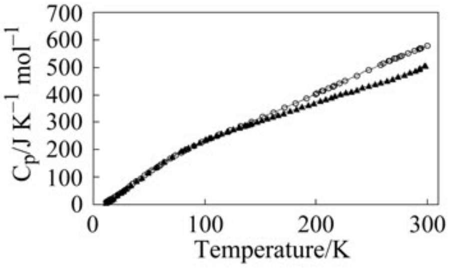

Fig. 2 Heat capacity of $Ni(NH_2trz)_3(NO_3)_2{\cdot}H_2O$ is shown by circles and $Cu(NH_2trz)_3(NO_3)_2{\cdot}0.5H_2O$ [1] is shown by triangles

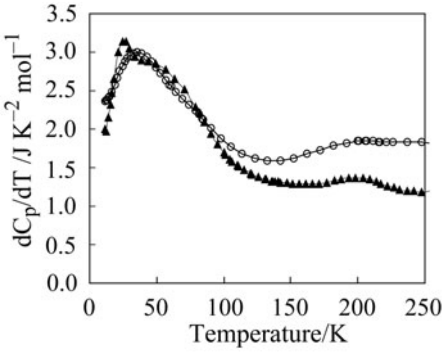

Fig. 3 The temperature derivative of heat capacity. Circles represent $Ni(NH_2trz)_3(NO_3)_2{\cdot}H_2O$ and triangles – $Cu(NH_2trz)_3(NO_3)_2{\cdot}0.5H_2O$ [1]

The curves $C_p(T)$ for both substances in the range 11–120 K are closely related. The distinction between them appears at T>~120 K and amount to 15% at 300 K. The analysis of the temperature derivatives of heat capacity shows, that there is an essential change of a regular shape of curves $C_p(T)$ for both substances. Figure 3 shows that the behavior of dC_p/dT changes considerably at T>115 K. Usually, the function dC_p/dT after a maximum at low temperatures, lowers gradually with increasing temperature, if the dependence $C_p(T)$ has no anomalies. In Fig. 3 one can see a considerable change of the slope of both curves dC_p/dT near 110–120 K. This implies that additional degrees of freedom appear or some process begins in both substances compared. It is not possible to establish the reason for such behavior of heat capacity basing on only low-temperature thermodynamic properties. Thus further researches seem necessary.

Conclusions

The temperature dependence of the heat capacity of $Ni(NH_2trz)_3(NO_3)_2 \cdot H_2O$ was investigated in the range from 11 to 317 K and the thermodynamic functions at 298.15 K were calculated on the basis of these data. It was found out, that the trend of the temperature derivative of heat capacity changes essentially at 110–120 K that is an additional contribution to the heat capacity appears at these temperatures.

The effect of diminution of the heat capacity of the sample down to zero in the interval from 5.5 to 11 K was observed when the pressure of heat exchanging helium in the calorimeter ampoule was $1.3 \cdot 10^3$ Pa. This effect is presumably connected with total absorption of gaseous helium by the sample at temperatures below 11 K.

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