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HEAT CAPACITY OF POLYNUCLEAR $Fe(HTrz)_3(B_{10}H_{10})\cdot H_2O$ AND TRINUCLEAR $[Fe_3(PrTrz)_6(ReO_4)_4(H_2O)_2](ReO_4)_2$ COMPLEXES (HTrz=1,2,4-triazole, PrTrz=4-propyl-1,2,4-triazole) manifesting $^1A_1\Leftrightarrow{}^5T_2$ spin transition

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Low-temperature heat capacity of polynuclear $Fe(HTrz)_3B_{10}H_{10}\cdot H_2O$ **(I)** and trinuclear $[Fe_3(PrTrz)_6(ReO_4)_4(H_2O)_2](ReO_4)_2$ **(II)** spin crossover coordination compounds was measured in 80–300 K temperature range using a vacuum adiabatic calorimeter. For **I**, an anomaly of heat capacity with a maximum at T_{trs}=234.5 K (heating mode) was observed, $\Delta_{trs}H$=10.1±0.2 kJ mol^{-1}, $\Delta_{trs}S$=43.0±0.8 J mol^{-1} K^{-1}. For **II**, a smooth anomaly between 150 and 230 K was found, $\Delta_{trs}H$=2.5±0.25 kJ mol^{-1}, $\Delta_{trs}S$=13.6±1.4 J mol^{-1} K^{-1}. Anomalies observed in both compounds correspond to $^1A_1\Leftrightarrow{}^5T_2$ spin transition.

Keywords: *heat capacity, iron coordination compounds, spin transition, triazole derivatives*

Introduction

Iron(II) coordination compounds having (pseudo)octahedral $[FeN_6]$ core providing by nitrogen containing ligands with intermediate ligand field strength often exhibit reversible spin transition between low-spin (LS, S=0, $^1A_1$) and high-spin (HS, S=2, $^5T_2$) states [1–5]. The transition can be induced by various external perturbations such as temperature variation, light irradiation, pressure or magnetic field. By now several theoretical model of spin transition were developed [6]. Nevertheless, microscopic mechanism of spin transition does not fully clear up to now. In this context, the studies of the main chemical and electronic factors responsible for the occurrence and the character of the spin transition are of importance to understand the peculiarities of mechanism of the transition.

Lavrenova *et al.* synthesized and studied a large number of polynuclear and trinuclear iron(II) coordination compounds with 4-substituted 1,2,4-triazoles (RTrz) of general formulae $Fe(RTrz)_3A_n\cdot mH_2O$ (n=1, 2) and $Fe_3(RTrz)_n(H_2O)_mA_6$ (n=6, 8; m=6, 4). Most of them exhibit $^1A_1\Leftrightarrow{}^5T_2$ spin transition accompanied by thermochromism. The character of the transition (completeness, sharpness and the temperatures of the direct ($T_c\uparrow$) and reverse ($T_c\downarrow$) transitions) depends substantially on the nature of the ligand and anion and the presence of solvent molecules in the structure of the compounds [7-10].

The first works dealing with heat capacity measurements of spin transition compounds were published in 1972–1974 by Sorai and Seki [11, 12] and Zelentsov *et al.* [13]. To measure heat capacities of complexes adiabatic calorimeters were used. Later Sorai with colleagues studied complexes with abrupt and gradual transitions, considered the influence of solvent on spin transition's character, examined solid solutions of complexes of two metals, etc. [14].

Earlier we presented the results obtained in studying the thermodynamic properties of several polynuclear spin transition iron(II) complexes on the base of 4-amino-1,2,4-triazole and 4-propyl-1,2,4-triazole [15–18]. Also we studied isobaric heat capacity dependence ($C_p(T)$) of trinuclear complex $[Fe_3(PyTrz)_8(H_2O)_4](NO_3)_6$, where PyTrz= 4-(2-pyridyl)-1,2,4-triazole, between 8 and 340 K [19]. It was found that $^1A_1\Leftrightarrow{}^5T_2$ spin transition in these compounds corresponds to phase transition and $\Delta_{trs}S$ for all of the compounds exceed purely electronic contribution $\Delta_{el}S$=13.38 J K^{-1} mol^{-1}.

Here we report results of isobaric heat capacity studies of two spin transition iron(II) complexes with 4-R-1,2,4-triazoles. The first is a polynuclear complex $Fe(HTrz)_3(B_{10}H_{10})\cdot H_2O$ **(I)** (HTrz=1,2,4-triazole). Spin transition for this compound is practically complete and abrupt with temperatures $T_c\uparrow$ and $T_c\downarrow$ derived from magnetochemical data being 246 and 233 K respectively, the width of the hysteresis loop is 13 K [20]. The second is a trinuclear complex

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$[Fe_3(PrTrz)_6(ReO_4)_4(H_2O)_2](ReO_4)_2$ (**II**) (PrTrz=4-propyl-1,2,4-triazole). In contrast to **I** the transition observed is gradual (but also complete) with temperature T_c~185 K (without hysteresis) [21]. In both compounds spin transition is accompanied by thermochromism (pink (LS)⇔white (HS) (**I**), yellow (LS)⇔white (HS) (**II**)).

Experimental

For the measurements, the samples of compounds **I** and **II** were obtained as described in [20, 21]. The isobaric heat capacity C_p of the complexes was measured on a vacuum adiabatic calorimeter with pulse heating. The calorimetric ampoule for samples was made of nickel (6 cm^3, mass 22.4 g). The temperature was measured by platinum resistance thermometer (R_0=50 abs. Ω). The mean deviation of the experimental heat capacity values from the smoothed curve for an empty ampoule was 0.1% over the temperature range 80–350 K. Control measurements of standard benzoic acid showed good agreement with the reference data [22]. The same calorimeter was used previously in [15–19].

Results and discussion

The heat capacity of complex **I** (sample mass 0.1811 g) was determined over the temperature range 85–300 K (Fig. 1), experimental C_p values are listed in Table 1. The heat capacity anomaly with maximum at T_{trs}=234.5 K corresponds to $^1A_1 \Leftrightarrow {}^5T_2$ spin transition ($T_c\uparrow$=246 K, $T_c\downarrow$=233 K). The standard deviation is about 3% above 250 K and about 1.5% below 200 K. It is explained by small amount of the sample (small contribution provided by a sample to the general heat capacity). The regular part of C_p in the area of anomaly can be estimated by different ways: a) by extrapolation (linear or by using of a polynom) of left and right branches of heat capacity to T_{trs} from areas which are far from area of anomaly; b) by using of dependence of Debye characteristic temperature, $\Theta_D(T)$, calculated from heat capacity. In this case one can extrapolate $\Theta_D(T)$ to T_{trs} by means of a polynom and then to calculate the dependence of C_p(reg). Both these methods give practically the same results when the enthalpy and entropy are calculated. We estimated C_p(reg) using Debye characteristic temperature since

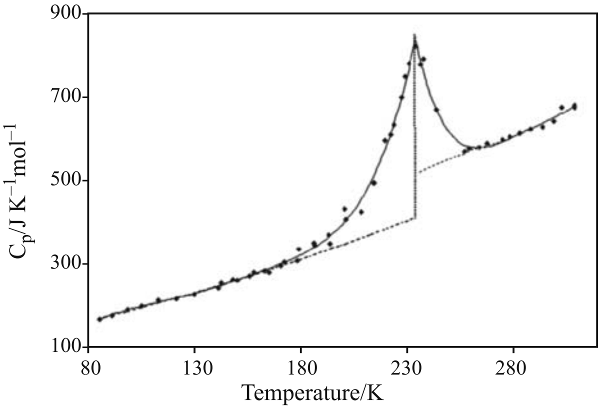

Fig. 1 Molar heat capacity of $Fe(HTrz)_3B_{10}H_{10}\cdot H_2O$ (**I**)

Table 1 Experimental values of heat capacity (J K^{-1} mol^{-1}) of $Fe(HTrz)_3B_{10}H_{10}\cdot H_2O$ (complex **I**); *M*=399.25 g mol^{-1}

T/K	C_p	*T*/K	C_p	*T*/K	C_p	*T*/K	C_p
Series 1		193.56	366.7	227.65	694.9	163.41	281.1
85.80	165.3	201.10	429.9	231.09	776.9	171.00	292.6
91.72	174.3	Series 3		234.50	817.3	178.92	306.5
98.59	189.9	214.76	491.4	237.88	787.5	186.66	342.9
105.57	196.8	222.40	606.6	Series 5		194.25	346.6
113.26	211.6	229.43	745.7	233.73	509.8	201.68	404.2
121.58	213.8	236.77	773.4	236.34	524.5	Series 7	
130.25	225.62	244.08	665.9	239.36	546.7	275.36	594.4
Series 2		250.90	561.6	244.48	550.3	278.97	600.2
142.68	252.8	257.66	565.6	251.66	554.5	283.33	609.0
150.47	260.1	264.31	576.0	259.58	572.4	288.43	619.8
158.02	278.5	Series 4		267.79	585.8	293.89	624.5
165.35	278.5	208.65	423.0	Series 6		299.31	637.2
172.50	304.3	214.49	492.0	141.45	240.4		
179.49	334.1	219.80	593.2	148.63	261.0		
186.34	349.4	224.17	626.8	156.13	269.2		

Table 2 Experimental values of heat capacity (J K^{-1} mol^{-1}) of $[Fe_3(PrTrz)_6(ReO_4)_2(H_2O)_2](ReO_4)_2$ (complex **II**); M=2371.69 g mol^{-1}

T/K	C_p	T/K	C_p	T/K	C_p	T/K	C_p
Series 1		154.31	1233	132.36	1080	291.43	1762
177.63	1366	159.48	1295	Series 4		296.24	1777
182.42	1411	164.56	1318	212.22	1535	301.00	1779
187.15	1433	169.54	1341	220.90	1559	Series 6	
191.81	1443	174.20	1379	229.89	1584	156.54	1264
196.41	1492	Series 3		238.71	1615	161.84	1287
200.96	1504	83.18	795.2	247.39	1634	167.54	1318
205.45	1529	87.83	839.4	256.38	1661	173.65	1355
210.37	1525	93.03	874.9	265.71	1708	179.63	1398
215.68	1536	98.46	899.4	Series 5		185.51	1435
Series 2		103.57	938.0	275.23	1702	191.30	1453
138.07	1129	108.90	964.4	278.93	1727	197.02	1465
143.62	1156	115.53	988.4	282.99	1751	203.12	1494
149.02	1192	123.90	1042	287.01	1771		

that this estimation allows to determine low-temperature border of the transition more precisely. The enthalpy of the transition was calculated from the extra contribution to heat capacity between 180 and 250 K, the value of enthalpy is 10.1±0.2 kJ mol^{-1}. The error is estimated taking into account a regular part approximation error in the area of anomaly and an average deviation of experimental values of C_p from the smoothed curve $C_p(T)$.

Entropy value was calculated as $\Delta_{trs}S=\Sigma(\Delta C_p\Delta T)/T_{middle}=43.0\pm0.8$ J K^{-1} mol^{-1}. This value exceed purely electronic contribution (for Fe(II) $\Delta_{el}S$= Rln5=13.38 J K^{-1} mol^{-1}) thus indicating substantial structure change contribution to $\Delta_{trs}S$. Heat capacity jump ΔC_p at T_{trs} equals 116 J K^{-1} mol^{-1} (Fig. 1). The first four points of a series 5 (Table 1) correspond to a supercooled high-spin phase of a complex. Presence of a temperature hysteresis allows to attribute phase transition observed to the first-order.

The heat capacity of complex **II** (sample mass 0.5910 g) was determined over the temperature range 83–300 K (Fig. 2), experimental C_p values are listed in Table 2. On a $C_p(T)$ dependence a very smooth anomaly between 150 and 300 K was observed. The maximum deviation of experimental data from the smoothed curve $C_p(T)$ is about 3%. A regular part of C_p was interpolated by polynom of 6 order. Enthalpy and entropy changes, connected with anomaly observed, calculated from $\Delta C_p= C_p(\text{exp.})–C_p(\text{reg.})$ dependence, are equal correspondingly 2.5±0.25 kJ mol^{-1} and 13.6±1.4 J K^{-1} mol^{-1}. The average error of experimental data is about 0.5% above 230 and below 150 K. In trinuclear complex **II** only central ion of iron(II) undergoes a spin transition, while two terminal iron(II) ions are in HS state [21]. The value of $\Delta_{trs}S$ obtained for a complex **II** is close to the purely electronic contribution caused by change of spin (13.38 J K^{-1} mol^{-1}). This indicates that structure changes in complex **II** when spin transition occurs are small and their contribution to $\Delta_{trs}S$ is negligible. The value of entropy obtained allows us to suggest that, in contrast to complex **I**, spin transition in trinuclear complex **II** occurs without substantial structure changes and has almost purely electronic nature. For other trinuclear complex $[Fe_3(PyTrz)_8(H_2O)_4](NO_3)_6$ with gradual spin transition between 170 and 260 K entropy value (15 J K^{-1} mol^{-1}) is also very close to purely electronic contribution [19].

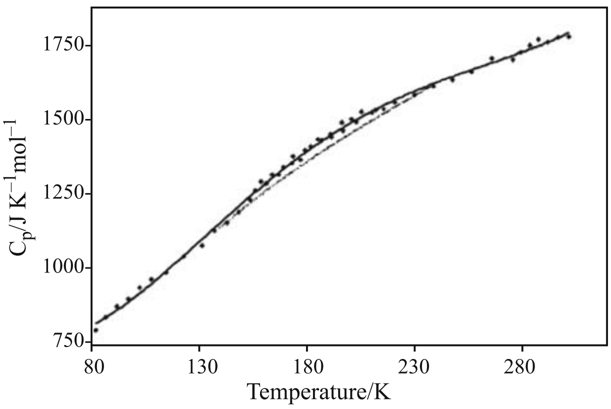

Fig. 2 Molar heat capacity of $[Fe_3(PrTrz)_6(ReO_4)_4(H_2O)_2](ReO_4)_2$ (**II**)

Conclusions

Thus, thermal dependence of isobaric heat capacity of $Fe(HTrz)_3B_{10}H_{10}\cdot H_2O$ and $[Fe_3(PrTrz)_6(ReO_4)_4(H_2O)_2](ReO_4)_2$ spin crossover complexes was studied. Anomalies of heat capacity connected with spin transition were observed for both compounds and $\Delta_{trs}S$ and $\Delta_{trs}H$ values were calculated. It was found that there present a substantial structure change contribution to $\Delta_{trs}S$ for complex $Fe(HTrz)_3B_{10}H_{10}\cdot H_2O$.

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