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Thermodynamic properties of dicarbonyl rhodium *o*-semiquinonate complex whose crystals display photomechanical properties

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Abstract

In an adiabatic low-pressure calorimeter, the temperature dependence of the standard molar heat capacity of paramagnetic dicarbonyl rhodium complex with *o*-semiquinone $(CO)_2Rh(SQ)$ has been determined in the range from $T = (6$ to $355)$ K mainly with an accuracy of about 0.3%. Over the ranges from $T = (205$ to $234)$ K, $T = (266$ to $315)$ K and $T = (316$ to $345)$ K physical transformations have been revealed and their enthalpies and entropies have been estimated. The experimental data were used to calculate the thermodynamic functions $C^{\circ}_{p,m}/R$, $\Delta^{T}_{0}H^{\circ}_{m}/(R \cdot K)$, $\Delta^{T}_{0}S^{\circ}_{m}/R$ and $\Phi^{\circ}_{m} = \Delta^{T}_{0}S^{\circ}_{m} - \Delta^{T}_{0}H^{\circ}_{m}/T$ (where R is the universal gas constant) between $T = (0$ and $355)$ K. The fractal dimension D in the heat capacity function of the fractal variant of Debye heat capacity theory has been evaluated.

Keywords: Paramagnetic dicarbonyl rhodium *o*-semiquinonate complex; Heat capacity; Thermodynamic functions; Thermodynamic parameters of physical transformations

1. Introduction

More than 20 years ago, the unique property of thread-like crystals of $(CO)_2Rh(3,6\text{-DBSQ})$, where 3,6-DBSQ is 3,6-di-*tert*-butyl-*o*-benzosemiquinone (an anion radical), to bend reversibly under light irradiation or thermal activation was observed. The maximum angles of bending, which were determined, exceeded 90°. The direction of bending does not depend on the direction of light irradiation, which excludes the bending because of warming of one of the crystal sides. The direction of bending is the specific property of each crystal. The maximum sensitivity lies in the NIR region and does not coincide with maxima of absorption [1].

The structural study indicated square-plane monomeric complex molecules [2]. Molecular planes are parallel, lay one over another and are stacked in a column through rhodium–rhodium bonds. Rhodium atoms form endless chain with alternating Rh–Rh distances 0.3252(4) nm and 0.3304(5) nm.

Magnetic measurements show the presence of both ferro- and antiferromagnetic interactions. The magnetic moment value indicates less than one electron per molecule. A sharp increase of the magnetic moment at $T = 105$ K was interpreted by the authors as ferromagnetic ordering [2]. A NIR spectrum of a solid sample of the complex demonstrates the lowest energy transition,

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centred at 1550 nm and reflecting a metal–ligand charge transfer [2].

The similar complex $(CO)_2Rh(3,6\text{-DBSQ-}4,5\text{-}(OMe)_2)$, as recently reported by the Japanese scientists [3], has very close structural features. Magnetic measurements point to ferro- and antiferromagnetic interactions. The authors observed the first-order phase transition at $T = 216$ K accompanied by an abrupt increase of $\chi_M T$ value with decreasing temperature.

The foregoing has stimulated the present study. Here we discuss the temperature dependence of the standard molar heat capacity $C^\circ_{p,m}$ of dicarbonyl rhodium complex with 3,6-di-*tert*-butyl-*o*-semiquinone determined in the adiabatic low-pressure calorimeter over the range from $T = (6$ to $355)$ K.

2. Experimental

A sample suitable for the calorimetric investigation was synthesized as described previously [1,2]. Recrystallization from *n*-hexane produces thin deep brown needles. Elementary analysis indicated (mass fraction) C 0.5085, H 0.0530 (calculated for $C_{16}H_{20}O_4Rh$ C 0.5067, H 0.0532). EPR and IR spectra, magnetic susceptibility data reproduce measurements described earlier [1,2].

For the measurement of $C^\circ_{p,m}$ of the compound in the temperature range of $T = (6$ to $355)$ K, a BKT-3 adiabatic low-pressure calorimeter with an automatic system of maintaining the adiabatic regime of measurements was employed. The calorimeter design and the operational procedure were similar to those described earlier [4]. The iron–rhodium thermometer used was calibrated by IST-90. The reliability of the calorimeter operation was tested by measuring the heat capacities of special-purity copper (OSCh 11-4), standard synthetic corundum [5] and K-1 benzoic acid [5] prepared at metrological institutions of the State Standard Committee of Russian Federation. It was established that the apparatus and the measurement procedure allowed us to obtain the $C^\circ_{p,m}$ values of the substances in a condensed state with an uncertainty of not more than 2% from $T = (6$ to $10)$ K, 0.5% between $T = (10$ and $40)$ K, and within 0.2% in the range $T = (40$ to $355)$ K.

The sample of dicarbonyl rhodium complex with *o*-semiquinone (0.2011 g) was placed in a calorimetric ampoule. After evacuating, the ampoule with the substance was filled with special-purity helium as a heat-exchange gas up to a pressure of 6 kPa (at room temperature) and sealed. The measurements of $C^\circ_{p,m}$ were made between $T = (6$ and $355)$ K and 244 experimental $C^\circ_{p,m}$ values were obtained in six series reflecting the sequence of the heat capacity measurements (table 1). Since the heat capacity of the complex (0.2011 g) placed in the calorimetric ampoule consisted in all about (20 to 30)% of

TABLE 1
Experimental molar heat capacities of dicarbonyl rhodium complex with *o*-semiquinone ($M = 379.238$ g · mol^{-1}, $R = 8.3144$ J · K^{-1} · mol^{-1})

T/K	$C^\circ_{p,m}/R$
Series 6	
6.44	0.356
6.96	0.460
7.40	0.534
7.81	0.602
8.22	0.674
8.63	0.782
9.08	0.842
9.59	0.962
10.06	1.022
10.53	1.129
10.99	1.221
11.44	1.317
11.89	1.418
12.48	1.537
13.21	1.696
13.93	1.861
14.75	2.063
15.46	2.227
16.17	2.387
16.87	2.562
17.56	2.726
18.26	2.889
18.96	3.061
19.65	3.235
21.36	3.676
23.81	4.289
26.26	4.877
28.73	5.516
31.18	6.139
34.00	6.822
36.50	7.374
38.58	7.800
41.08	8.287
43.58	8.792
46.08	9.306
48.58	9.789
51.08	10.25
53.60	10.76
56.09	11.26
58.80	11.84
61.12	12.29
63.62	12.81
66.11	13.35
68.61	13.87
71.11	14.37
73.80	14.93
76.11	15.36
78.62	15.87
81.12	16.37
Series 1	
83.75	16.88
86.62	17.61
89.08	18.10
91.53	18.47
93.99	18.84
96.45	19.20
98.89	19.61
101.34	19.98

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