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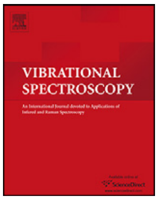

Calorimetric and vibrational spectroscopic investigations of phase transitions in crystalline $[Cr(OS(CH_3)_2)_6](BF_4)_3$

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ABSTRACT

Two phase transitions – one sharp at $T_1 = 247.4$ K and the other very broad at $T_2 \sim 135$ K – were observed for $[Cr(OS(CH_3)_2)_6](BF_4)_3$ by adiabatic calorimetry. They are of the order–disorder type, and their transition entropies are 28.4 and 8.3 J K^{-1} mol^{-1}, respectively. IR absorption and Raman scattering spectroscopy measurements revealed distinct changes in the molecular dynamics of both CH_3 groups and BF_4^- anions at T_1 and reduced symmetry of the $[Cr(OS(CH_3)_2)_6]^{3+}$ complex cations and $OS(CH_3)_2$ ligands below T_2. The spectral width of an IR and Raman active band associated with the $\delta_{as}(FBF)F_2$ mode yielded an activation energy (E_a) ~ 9 kJ mol^{-1} for the reorientation of BF_4^- anions, which is comparable with that obtained for other coordination compounds with BF_4^- anions.

1. Introduction

Dimethyl sulfoxide ($OS(CH_3)_2$, DMSO) is a versatile compound used as a solvent in various organic syntheses and also acts as a ligand in coordination chemistry. In liquid, the molecules form stable dimers which are held together by weak intermolecular C—H···O interactions and long-range electrostatic attraction between oxygen and sulfur deriving from adjacent dipoles [1,2]. When attached to a metal ion in coordination compounds, DMSO can form bonds *via* oxygen or sulfur atom depending on a type of metal based on Lewis classification [3,4]. The oxygen-coordinated ligands are often disordered especially with symmetric anions such as BF_4^-, which causes difficulties in determination of the crystal structure. In such cases vibrational spectroscopy is an important tool to identify the molecular structure and dynamics of particular species and their interactions across temperature.

Thermal behavior of coordination compounds with DMSO ligands coordinated octahedrally to transition metals and with tetrahedral BF_4^- uncoordinated anions has been investigated for three crystalline compounds – $[Ni(DMSO)_6](BF_4)_2$, $[Co(DMSO)_6](BF_4)_2$, and $[Mn(DMSO)_6](BF_4)_2$ – by differential scanning calorimetry (DSC) [5–7]. These compounds are characterized by solid polymorphism above room temperature with several phase transitions occurring between both stable and metastable phases. $[Mn(DMSO)_6](BF_4)_2$ undergoes an additional phase transition at 215 K accompanied by a small entropy change $\Delta S = 1.3$ J K^{-1} mol^{-1} [7]. However, except for the spectroscopic analysis at room temperature, there is no information concerning the phase behavior of any analogous compounds with trivalent central metals. The compound that we study here – $[Cr(DMSO)_6](BF_4)_3$ (hereafter referred to as CrHB) – exhibits a completely different thermal behavior from others. As described below, we observed two transitions at $T_1 = 247.4$ K and $T_2 \sim 135$ K, both accompanied by a large entropy change. Interestingly, similar phase transitions were observed for $[Cr(NH_3)_6](BF_4)_3$ [8] at nearly the same temperatures.

This study precisely examines the phase behavior of CrHB between 5 and 300 K using adiabatic calorimetry and two complementary spectroscopic methods: Fourier-transform infrared absorption and Raman light scattering. We discuss the possible mechanism of the phase transitions.

2. Experimental

2.1. Materials

First, 2 g of $Cr(NO_3)_3 \cdot 9H_2O$ (Kanto Chem. Co. Inc.) was dissolved in about 15 mL of distilled water and then 5 mL of 40% HBF_4 solution (Wako Pure Chem. Ind. Ltd.) was added. A polypropylene temperature resistant beaker was used. Next, the solution was slowly

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heated up to evaporate the excess solvent and then chilled to room temperature and fine green crystals of $Cr(BF_4)_3 \cdot xH_2O$ were precipitated and dried over phosphorus(V) oxide (P_4O_{10}). The crystals obtained were dissolved during heating in anhydrous DMSO (99.5%, Wako Pure Chem. Ind. Ltd.). The solution was chilled to room temperature and a green powder of $[Cr(OS(CH_3)_2)_x](BF_4)_3$ precipitated, where $x = 2–6$. To obtain the compound with the appropriate coordination, it was recrystallized four times from DMSO with final percent yield value of more than 70%. The final compound CrHB is hygroscopic; therefore, it was placed in a sealed vessel and stored in a desiccator over P_2O_{10}. Its composition was determined by elemental analysis on a EURO EA 3000 instrument based on the C and H content of the DMSO ligands. Theoretical contents: C, 18.45%; H, 4.64%. Found: C, 18.41%; H, 4.50%.

2.2. Methods

Heat capacity measurements were carried out between 5 and 300 K using a laboratory-made adiabatic calorimeter. As a sample is hygroscopic it was placed in a gold-plated copper cell with an inner volume of 2.77 cm^3 and sealed under a helium atmosphere and then weighed. The sample mass was 1.5111 g after buoyancy correction. The temperature was measured with a rhodium–iron alloy resistance thermometer. The heat capacity of the empty cell was measured in advance and subtracted from the total heat capacity. The dead space of the sample cell was filled with helium gas at ambient pressure to advance equilibration. More details concerning this experiment can be found in previous papers [9,10]. Additional calorimetric measurements were also performed by DSC between 300 and 400 K to confirm that no phase transition exists above 300 K.

Fourier-transform far-infrared (FT-FIR) and Fourier-transform mid-infrared (FT-MIR) absorption measurements were performed using BIO-RAD FTS-40V and JASCO FT-IR-6100 spectrometers, respectively. The room temperature FT-FIR spectrum was recorded at 40–500 cm^{-1} with a resolution of 2 cm^{-1}. The sample was suspended in paraffin wax and placed between polyethylene windows. FT-MIR spectra were obtained at 500–4000 cm^{-1} with a resolution of 2 cm^{-1} using a liquid helium cryostat. Two samples – one suspended in Nujol and the other in Fluorolube – were prepared and placed between two KBr plates. The sample in Fluorolube was measured during cooling from 300 K down to 15 K and the sample in Nujol was measured during heating from 15 K up to 285 K, both under vacuum conditions. The temperature stabilization accuracy was ±1 K.

Raman scattering (RS) measurements were performed with a JASCO NR-1800 spectrometer with a resolution of 2 cm^{-1}. The incident radiation ($\lambda = 1064$ nm) came from a Nd:YAG laser (Spectra-Physics). All spectra were recorded in the Raman shift range of 50–4000 cm^{-1} while cooling the sample from 300 K to 30 K using a liquid helium cryostat and under vacuum conditions.

3. Results and discussion

3.1. Calorimetric investigations

Fig. 1 illustrates the molar heat capacity of CrHB obtained by adiabatic calorimetry. The data are given in Supplementary information (Table S1). The compound exhibits a sharp phase transition at $T_1 = 247.4$ K, where the shape of the anomalous heat capacity curve is rather symmetric, tailing to the both temperature sides. The enthalpy of transition was evaluated by estimating a "normal" heat capacity curve, as indicated in Fig. 1. The enthalpy was 6.96 kJ mol^{-1}, and the corresponding entropy of transition was 28.4 J K^{-1} mol^{-1}. As shown in the inset of Fig. 1, where the heat capacity is plotted in the form of C_pT^{-1} against T, another phase transition was observed with a maximum at $T_2 \sim 135$ K. While this transition is very broad, the shape of the heat capacity anomaly is still symmetric. The enthalpy of transition was 1.03 kJ mol^{-1}, and the corresponding entropy was 8.3 J K^{-1} mol^{-1}. Fig. 2 illustrates the temperature dependence of the cumulative entropy due to the phase transitions. A two-step sigmoidal curve with a large entropy change is evident, suggesting that both transitions are of the order–disorder type. The total entropy amounted to 36.7 J K^{-1} mol^{-1}, demonstrating that the compound at 300 K is highly disordered.

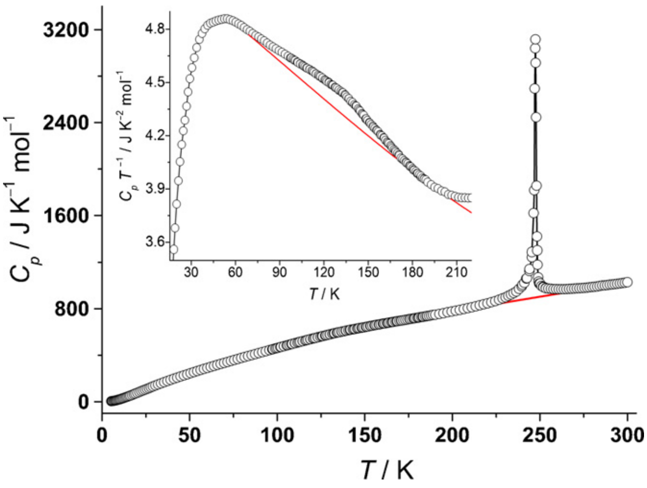

Fig. 1. Molar heat capacity C_p obtained for $[Cr(DMSO)_6](BF_4)_3$. Inset: plotted in the form of C_pT^{-1} against T. Baseline for the phase transitions is shown.

3.2. Spectroscopic investigations (FT-IR and RS spectra)

Table 1 presents a list of IR and Raman band positions, their relative intensities, and assignments denoted by comparison with the literature data for several $[M(DMSO)_6]X_3$ complexes and liquid DMSO [11–15]. There is no crystallographic data available for this particular compound, but the crystal structures of $[Cr(DMSO)_6]Cl_3$, $[Cr(DMSO)_6](NO_3)_3$, and $[Cr(DMSO)_6](ClO_4)_3$ obtained at room temperature show that the complex cation $Cr(DMSO)_6{}^{3+}$ has an octahedral symmetry with DMSO ligands coordinated to the central metal Cr^{3+} through oxygen atoms [16–18]. Moreover, the IR

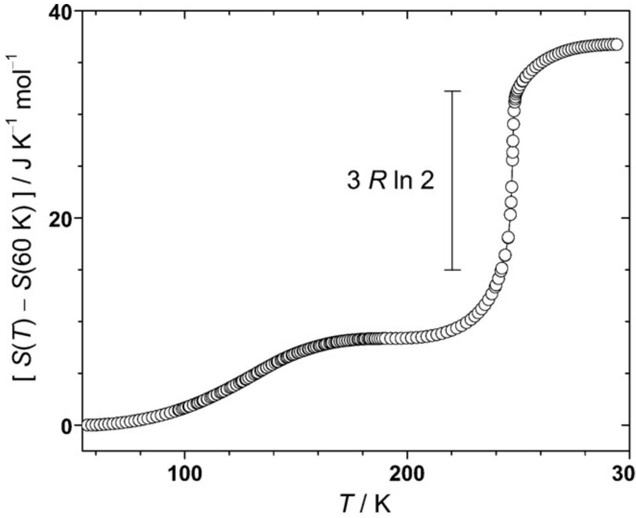

Fig. 2. Cumulative entropy across the two phase transitions. The size of 3R ln 2 is shown.