Thermoanalytical and Mass Spectrometric Study of Ni(iso-Bu₂PS₂)₂ and NiL(iso-Bu₂PS₂)₂ (L = 2,2'-Bipy, Phen). Saturation Vapor Pressure over the Ni(iso-Bu₂PS₂)₂ Chelate

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Abstract—The thermal behaviors of the chelate Ni(iso-Bu₂PS₂)₂ (I) and the mixed-ligand complexes Ni(2,2'-Bipy)(iso-Bu₂PS₂)₂ (II) and Ni(Phen)(iso-Bu₂PS₂)₂ (III) in air are reported. These compounds can pass into the gas phase, as was demonstrated by vacuum sublimation for I and by vacuum distillation for II and III in a gradient furnace. The mass spectra of I–III are presented and discussed. The temperature dependence of the saturation vapor pressure over I and ΔH° and ΔS° of evaporation of I determined by the vapor transport method are reported.

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The thermal decomposition of many 3d-metal chelates with organic ligands containing a CS₂ or PS₂ group yields a metal sulfide [1–5]. The said chelates containing certain alkyl substituents can pass into the gas phase when heated in vacuo. This fact has generated keen interest in the growth of metal sulfide films from these precursors by chemical vapor deposition [6–8]. Mixed-ligand complexes containing an ROCS₂ or R₂NCS₂ ion (particularly one with R = branched alkyl) or iso-Bu₂PS₂ and an uncharged ligand, such as 2,2'-bipyridine (2,2'-Bipy) and phenanthroline (Phen), are also capable of subliming [9–11]. Earlier, we synthesized the complexes Co(iso-Bu₂PS₂)₂ and ML(iso-Bu₂PS₂)₂ (M = Co(II), Mn(II); L = 2,2'-Bipy, Phen), studied their structure and thermal behavior, and examined their mass spectra [12, 13]. It is now interesting to study the properties of the Ni(II) analogues of these compounds, which are potential precursors of NiS films. It was demonstrated that NiS₁₁₀ and NiS + NiS₁₁₀ films can be obtained from nickel(II) dialkylthiocarbamates [14]. In industry, NiS is widely used as a hydorefining catalyst. NiS is also known to be a selective catalyst for diene hydrogenation into monoolefins [15, 16].

Here, we report a thermoanalytical and mass spectrometric study of the chelate Ni(iso-Bu₂PS₂)₂ and the mixed-ligand complexes Ni(2,2'-Bipy)(iso-Bu₂PS₂)₂ and Ni(Phen)(iso-Bu₂PS₂)₂ and the temperature dependence of the saturation vapor pressure over Ni(iso-Bu₂PS₂)₂.

EXPERIMENTAL

The synthesis of the chelate Ni(iso-Bu₂PS₂)₂ (I) and mixed-ligand complexes Ni(2,2'-Bipy)(iso-Bu₂PS₂)₂ (II) and Ni(Phen)(iso-Bu₂PS₂)₂ (III) was described earlier [17, 18]. For I, tₘ = 70–71°C. Compounds II and III apparently decompose without melting. The melting point was determined using a Boetius hot stage.

Thermoanalytical (DTA, TG, DTG) profiles for compounds I–III in air were recorded on a Paulik-Paulik-Erdey thermoanalytical system using quartz crucibles (heating rate of 2.5 K/min, Al₂O₃ reference, sample size of 50 mg). Based on thermoanalytical data, we chose temperatures for mass spectrometric evaluation of the volatility of I–III and for measuring the saturation vapor pressure over I as a function of temperature.

The mass spectra of complexes I–III were recorded on an MX-1310 mass spectrometer. Samples were introduced directly into the ion source. The evaporation temperature was 150°C for I and 170°C for II and III. The other mass spectrometric conditions were the same for all samples (Eᵢₒᵣ = 60 eV, p = 1 × 10⁻⁷ Torr).

The capacity of compounds I–III to pass into the gas phase was evaluated by vacuum distillation (chelate I) or vacuum sublimation (compounds II and III) in a gradient furnace (p = 1 × 10⁻¹–1 × 10⁻² Torr). The hot zone temperature was set so that the substance condensed on the tube surface 5–10 cm away from the sample boat. As chelate I was heated, it underwent distillation above 200°C. Most of the chelate evaporated at ~210–220°C, and the vapor condensed at ~180–
150°C (crystallization took place as the furnace was cooled). The greater part of complexes \( \text{II} \) and \( \text{III} \) sublimed at \( \sim 220–230°C \), and their vapor condensed at \( \sim 190–160°C \). The X-ray diffraction patterns of the resulting solid phases and those of initial complexes \( \text{I} \)--\( \text{III} \) coincided. The yields of \( \text{I} \), \( \text{II} \), and \( \text{III} \) after distillation (sublimation) were 98, 96, and 97%, respectively. For chelate \( \text{I} \) that resulted from distillation, \( t_m = 66°C \).

The temperature dependence of the saturation vapor pressure over chelate \( \text{I} \) (predistilled in the gradient furnace) was studied by the vapor transport method under quasi-equilibrium conditions using helium as the carrier gas [19]. Dry helium (flow rate of 0.5–2.0 L/h) was passed through a bulk source of \( \text{I} \) maintained at a preset temperature. The mass of the initial sample and the mass of the solid condensed in the cold zone were determined by weighing. The nickel content of the condensate was determined chelatometrically, and it was found that only \( \sim 80\% \) of the initial chelate \( \text{I} \) evaporated and condensed without decomposition. For this reason, the necessary corrections were applied in the calculation of the saturation vapor pressure. The saturation vapor pressure was calculated via the formula

\[
p_0 = \frac{p_{\text{total}} n}{n + N},
\]

where \( n \) is the number of moles of the substance transferred, \( N \) is the number of moles of the carrier gas, and \( p_{\text{total}} \) is the total pressure in the system. The experimental error in this method did not exceed \( \pm 5\% \), and the temperature measurement error was \( \pm 0.5 \, \text{K} \).

RESULTS AND DISCUSSION

According to X-ray crystallographic data, the Ni atom and the four S atoms of the bidentate cyclic ligands iso-Bu₂PS₂ in mononuclear chelate \( \text{I} \) form a square-planar \( \text{NiS}_4 \) coordination entity [20]. The crystal structures of mixed-ligand complexes \( \text{II} \) and \( \text{III} \) are also built from mononuclear molecules [17, 21]. The Ni atom in these compounds has a distorted octahedral coordination sphere consisting of two N atoms and the four S atoms of the bidentate cyclic ligands. According to TG data, as complexes \( \text{I}--\text{III} \) are heated in air, \( \text{I} \) and \( \text{II} \) lose weight smoothly in one step, while \( \text{III} \) loses weight in two steps (Figs. 1–3, Table 1). The onset temperature of weight loss for \( \text{III} \) is somewhat higher than for \( \text{I} \) and \( \text{II} \). For chelate \( \text{I} \), the endotherm in the DTA curve is due to melting. The weight of the solid residues resulting from the thermolysis of \( \text{I}--\text{III} \) in air under the thermoanalytical conditions is not equal to the calculated NiS content of these compounds (Table 1). It is likely that oxidation by atmospheric oxygen takes place at high temperatures, so the decomposition product can contain NiSO₄, NiHPO₄, and NiO. To rule out the oxidation processes, samples of \( \text{I} \) and \( \text{II} \) were held at 400–420°C in an argon atmosphere for 2 h (Table 1). The weight of the solid residue obtained from \( \text{I} \) under these conditions was nearly equal to the calculated NiS content. According to X-ray diffraction data, the products of chelate \( \text{I} \) thermolysis in argon were NiS and Ni₂P.

Table 2 presents mass spectrometric data for the gas phase of chelate \( \text{I} \). The spectrum shows a strong peak due to the molecular ion [Ni(iso-Bu₂PS₂)₂]⁺ from the