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Thermodynamic Characteristics of Neodymium and Terbium Pyrazolonate Complexes

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Abstract—The sublimation of 1-phenyl-3-methyl-4-isobutyryl-5-pyrazolonate complexes of neodymium and terbium was studied by the Knudsen effusion method with mass spectrometric gas phase monitoring. The gas phase was shown to contain only monomeric molecular species. The sublimation enthalpy (kJ/mol) for Nd complex is 205.9 ± 2.7 and that for the Tb complex is 208.0 ± 4.0.

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INTRODUCTION

The interest in the chemistry of coordination compounds of lanthanides is due to their applicability as emission layers in OLED devices [1, 2]. Film coatings are often prepared by the MOCVD method. This method is characterized by effective control of deposition parameters and, thus, it provides the possibility for preparing layers and nanostructures with specified characteristics. The key role in the deposition processes of films and coatings is played by the precursor chemical used. The deposition of coatings with specified properties is related to gaining quantitative data on the structural, thermal, and thermodynamic characteristics of precursors. The search for materials for electro-optical converters has attracted attention to lanthanide complexes with pyrazolone ligand attached to the metal by a β-diketonate group.

Analysis of the published data demonstrated that no quantitative estimates of the volatility or thermodynamic characteristics of these compounds are available [3].

The purpose of this work was to measure the temperature dependences of the saturated vapor pressure and sublimation of neodymium and terbium pyrazolonate complexes of two types: amorphous $Ln(PMIP)_3$ (Ln = Tb (**I**)) and crystalline dimeric complexes $[Ln(PMIP)_3]_2$ (Ln = Nd (**II**), Tb (**III**)). Also, thermodynamic parameters of melting for compounds **II** and **III** were determined.

EXPERIMENTAL

Pyrazolonate complexes **I–III** were synthesized from pyrazolone and lanthanide in THF in the presence of a catalytic amount of LnI_3 [4]. After separation of the excess of the metal and removal of solvent, the compounds were heated for 3 h at 373 K in vacuum. This gave white amorphous powders with the composition given by $Ln(PMIP)_3$ (Ln = Nd, Tb; PMIP = 1-phenyl-3-methyl-4-isobutyryl-5-pyrazolonate). After sublimation in vacuum (10^{-3} Torr) at 230–265°C, the amorphous products were converted to binuclear crystalline complexes $[Ln(PMIP)_3]_2$ (Ln = Nd, Tb), which were studied by X-ray crystallography [4].

Compounds **II** and **III** were studied on a DSC204F1 Phoenix differential scanning calorimeter (Netzsch Gerätebau, Germany). The design of the calorimeter and the procedure of the work were reported [5, 6]. The reliability of the calorimeter operation was verified by standard calibration experiments in which the thermodynamic characteristics of melting were measured for cyclohexane, mercury, indium, tin, lead, bismuth, and zinc. These experiments demonstrated that the equipment and the procedure of measurements are suitable for determining the phase transition temperatures to an accuracy of ±0.5°C and determining the transition enthalpies to an accuracy of ±1%. The measurements were performed under argon at a heating rate of 5°C/min.

Determination of the saturated vapor pressure with mass-spectrometric monitoring of the gas phase composition and mass spectrometric analysis of the vapors of $[Ln(PMIP)_3]_2$ complexes were carried out by the reported procedure [7]. The measurements were done with an APDM-1 monopole mass analyzer modified for operation of molecular beams with masses up to 2500 amu and on an MI-1201 mass spectrometer adapted for thermodynamic measurements. The ionizing electron energy was 20–50 eV.

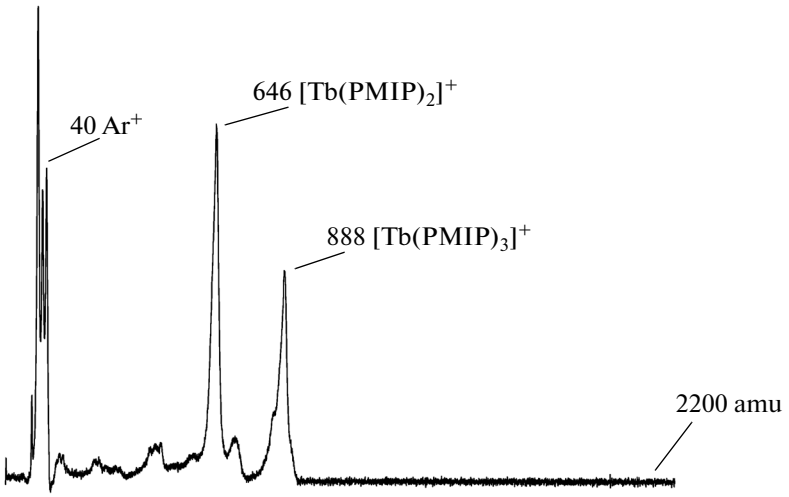


Fig. 1. Mass spectrum of a saturated vapor of $Tb(PMIP)_3$ recorded on an electron diffractometer/mass spectrometer setup at an ionizing voltage of 50 eV.

Saturated vapors of the compounds were studied using a molybdenum effusion cell with a vaporization area/effusion orifice area ratio of 500 for the APDM-1 instrument and 1000 for the MI-1201 instrument. The cell temperature was measured by a BP-5/20 tungsten–rhenium thermocouple calibrated against the melting points of tin, aluminum, and silver. The error of temperature measurement was not more than 3°C.

RESULTS AND DISCUSSION

The properties of complexes **II** and **III** in the temperature range of 25–350°C were studied by DSC. An endothermic transition associated with melting was revealed. The thermodynamic parameters of melting are presented below:

Complex	T_m, K	Range, K	ΔH, kJ/mol
II	213.5	213.5–221.5	164.2
III	237.0	237.0–246.0	201.0

The temperature of the onset of transition was taken as T_m according to the standard procedure of Netzsch Software Proteus. Preliminary experiments were carried out on a low-resolution APDM-1 mass spectrometer included in an electron diffractometer/mass spectrometer setup. The instrument covers the 1–2500 amu range of mass numbers.

Table 1. Mass spectrum of saturated vapors of $Tb(PMIP)_3$ and $Nd(PMIP)_3$*

Ions	Intensity, rel. %	
$[Ln(PMIP)_3]^+$	100.0	100.0
$[Ln(PMIP)_2]^+$	83	88.7
$[Ln(PMIP)_3\text{-}3CH_3]^+$	16	11.7

* $U_{ioniz} = 30$ eV. $T_{exp} = 526(5)$ (Tb) and 518(5) K (Nd).

The survey mass spectrum (Fig. 1) shows that in the 40–2200 range of mass numbers, the heaviest ion for **III** has $m/e = 888$. No dimers or heavier volatile species were detected.

The subsequent experiments were carried out on a MI-1201 commercial instrument, also modified for thermodynamic measurements. The instrument provided reliable coverage of mass numbers up to 1400 amu. Three experiments were carried out, one with an amorphous sample of **I** and two with the dimerized condensed phase of **III**. The mass spectra of the gas phase were the same for all three experiments. The mass spectra of the saturated vapor of **II** also had good repeatability in two experiments.

The mass spectra of the vapors of these compounds are shown in Fig. 2 and in Table 1. It can be stated with confidence that the saturated vapors of **II** and **III** contain only monomeric molecular species.

The origin of the fragment ions was elucidated by recording the mass spectra at different ionizing voltages. When $U_{ioniz} = 50$ eV, most intense was the ion current of $[LnL_2]^+$ where Ln is the lanthanide atom and L is the PMIP ligand. As the ionizing electron energy decreases, the ion current intensity of fragment ions also decreases: for $U_{ioniz} = 30$ eV, the ion current of the $[LnL_3]^+$ molecular ions prevails, while at $U_{ioniz} = 20$ eV, almost no fragment ions are recorded in the mass spectra.

For the molecular ions and the ions resulting from elimination of three methyl groups and one ligand, the theoretical and experimental isotope distributions are in full agreement. This is exemplified in Fig. 3, which

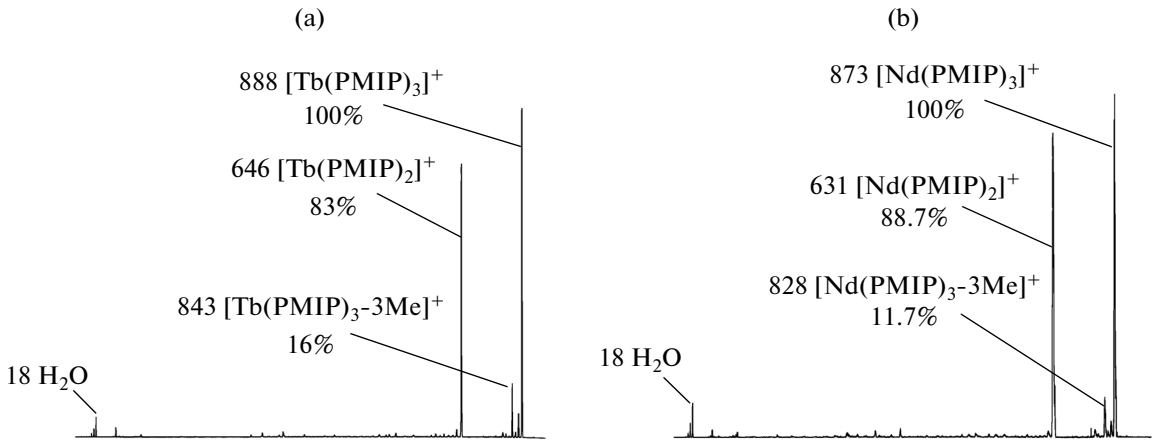


Fig. 2. Mass spectra of saturated vapors of (a) $Tb(PMIP)_3$ and (b) $Nd(PMIP)_3$ recorded on an MI-1201 mass spectrometer at an ionizing voltage of 30 eV.

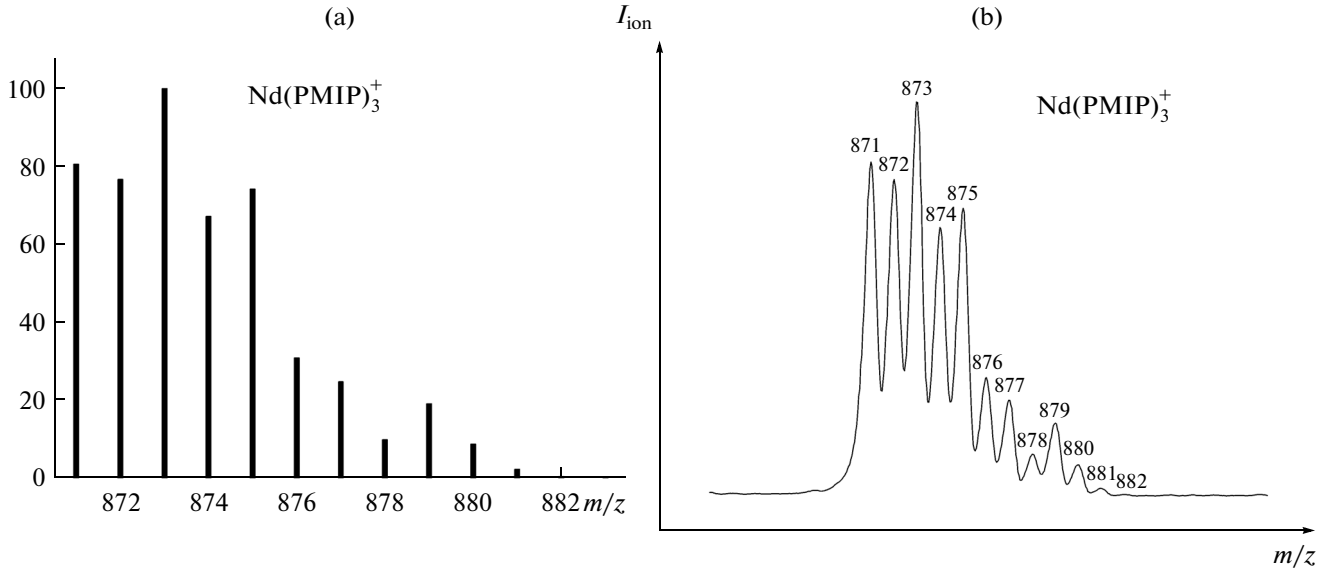


Fig. 3. (a) Theoretical and (b) experimental isotopic structure for the $Nd(PMIP)_3^+$ ion.

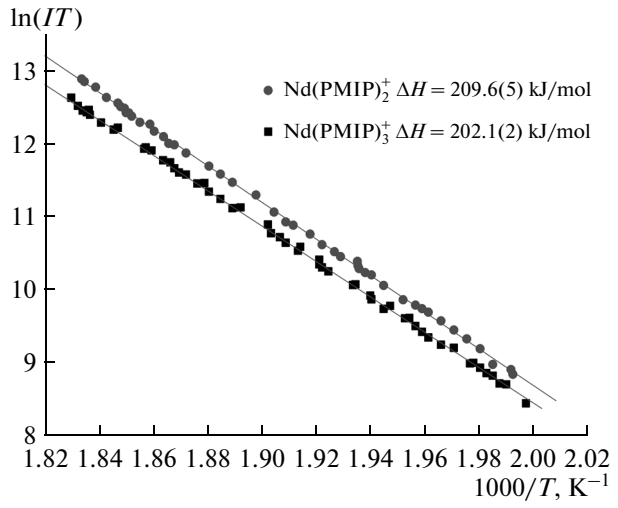
shows the calculated and the experimentally determined isotope distributions for the molecular ion in the mass spectrum of $Nd(PMIP)_3$.

For the molecular ions in the mass spectra of each compound, the dependences $\ln(IT) = f(1000/T)$ [8] were constructed, which are shown in Figs. 4–6. The points in these plots correspond to near-equilibrium states because no hysteresis was observed upon temperature increase/decrease. The experimental functions are well approximated by straight lines, which attests to thermal stability of these complexes in the gas phase in the given temperature range.

Determination of the sublimation enthalpies with mass-spectrometric monitoring of the gas phase composition was performed in terms of the Second Law of Thermodynamics based on the Clausius–Clapeyron equation by linear regression. Since the temperature

Table 2. Sublimation enthalpies of $Tb(PMIP)_3$, $[Tb(PMIP)_3]_2$, and $[Nd(PMIP)_3]_2$ according to a series of experiments on a MI-1201 mass spectrometer

Sample	Ions	$\Delta_{subl}H°(T)$, kJ/mol	
I	$Tb(PMIP)_2^+$	211.6(2.4)	
	$Tb(PMIP)_3^+$	207.6(2.0)	
II	$Nd(PMIP)_2^+$		209.2(2.3)
			202.1(2.1)
	$Nd(PMIP)_3^+$		209.7(1.6)
			202.7(3.9)
III	$Tb(PMIP)_2^+$	211.1(2.4)	
		205.3(3.5)	
	$Tb(PMIP)_3^+$	210.8(3.9)	
		206.8(3.6)	
Average		208.9(4.0)	205.9(2.7)



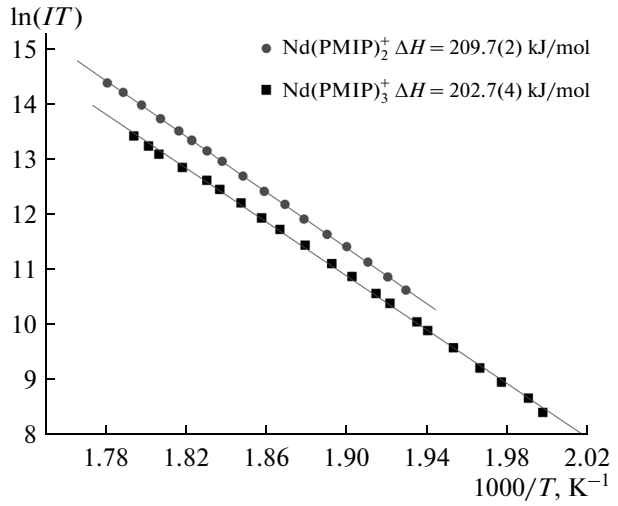
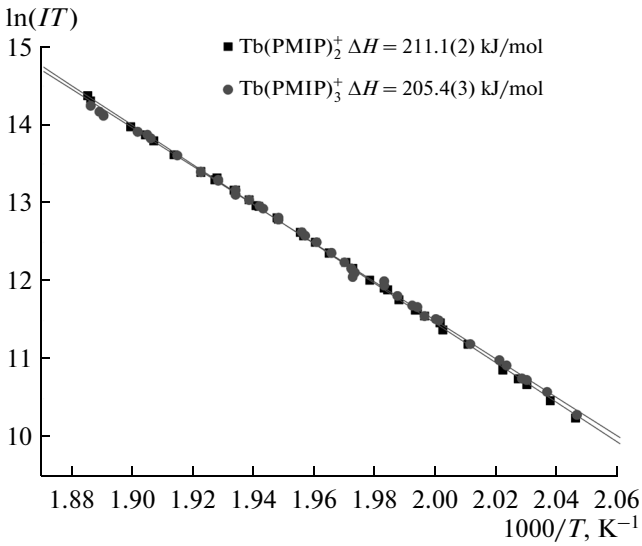


Fig. 4. Temperature dependences of the main ion currents in the mass spectra of $[Nd(PMIP)_3]_2$ recorded in two independent experiments under identical conditions using the same specimen.



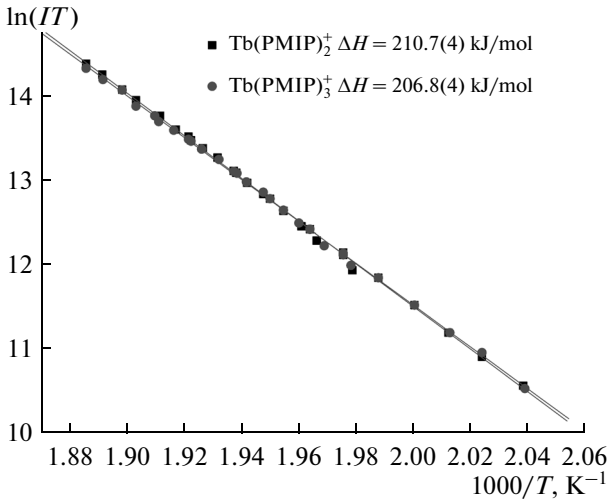


Fig. 5. Temperature dependences of the main ion currents in the mass spectra of $[Tb(PMIP)_3]_2$ recorded in two independent experiments under identical conditions upon sublimation of the condensed phase of the complex.

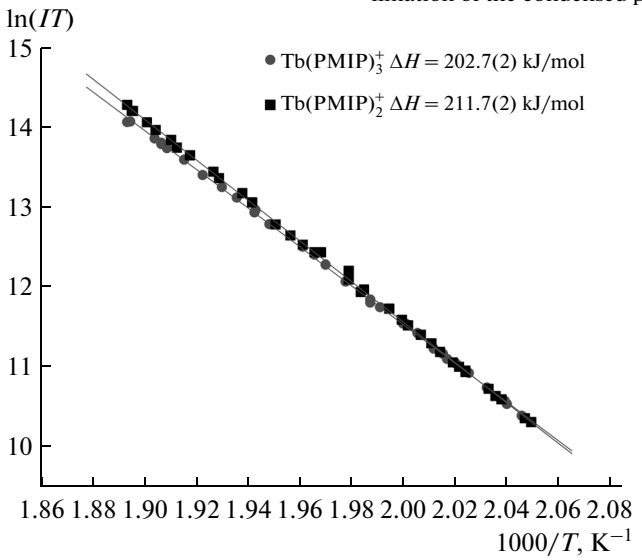


Fig. 6. Temperature dependences of the main ion currents in the mass spectra of amorphous $Tb(PMIP)_3$ recorded upon sublimation of the condensed phase of the complex.

range of measurements was relatively narrow, the enthalpy was assumed to be temperature-independent. The sublimation enthalpies of **I–III** are summarized in Table 2.

The sublimation enthalpies of **II** and **III** are close, which attests to comparable crystal lattice energies.

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