Sublimation Behavior of Tris(2,2,6,6-tetramethyl-3,5-heptanedionato)lanthanoid(III)

Ryohei Amano,* Akiko Sato,** and Shin Suzuki**
School of Paramedicine, Kanazawa University, Kodatsuno 5, Kanazawa 920
***The Research Institute for Iron, Steel and Other Metals, Tohoku University, Katahira 2, Sendai 980*

(Received June 20, 1980)

Two fundamental experiments (to determine vapor pressures and vacuum sublimation-recrystallizing temperature zones) were undertaken on a series of remarkably volatile and thermally stable lanthanoid(III) chelates of 2,2,6,6-tetramethyl-3,5-heptanedione (Ln(thd)$_3$) in order to obtain information about their sublimation behavior. Vapor pressures of these chelates were measured from 100 to 150 °C by means of a modified Knudsen effusion technique. Vacuum sublimation-recrystallizing temperatures were determined by using a sublimation apparatus with a continuous temperature gradient along its sublimation tube. The obtained enthalpies of sublimation were classified into three groups (La to Gd, Tb and Dy, and Ho to Lu), and the vacuum sublimation-recrystallizing temperature zones were divided into two sets (La to Tb, and Dy to Lu). The Tb and Dy chelates were also found to change thermally from a dimeric form to a monomeric form at a definite temperature. These results are explained in terms of the two different crystallizing forms of Ln(thd)$_3$ chelates. Furthermore, the regularity in their sublimation behavior is discussed as a function of the atomic numbers of the lanthanoid metals, using thermochemical considerations.

The volatile lanthanoid chelates of 2,2,6,6-tetramethyl-3,5-heptanedione are very useful as gasoline antiknock additives and catalysts for the removal of carbon deposits,[1] and as sources of metal chelate vapors.[2] They are also useful in trace metal analysis by gas chromatography and sublimatography.[3-5] It is therefore important to study the thermal properties of these chelates over a wide temperature range. Sicre *et al.* have determined the vapor pressures of the Ln(thd)$_3$ chelates (Ln=lanthanoid ion, thd=2,2,6,6-tetramethyl-3,5-heptanedione) by means of the isoteniscope technique over the temperature range of 150 to 250 °C and have mentioned the regularity in their thermochemical behavior.[4] Radiochemical studies on the Ln(thd)$_3$ and An(thd)$_n$ (An=actinoid ion) have been carried out by vacuum sublimation method; their sublimation-recrystallizing temperature zones were found to be in the range of 70 to 150 °C.[6] These vacuum sublimatographic results prompted us to study the vapor pressures of these chelates over the temperature range lower than 150 °C.

A modified Knudsen effusion method has been chosen for the measurements of vapor pressures of Eu(thd)$_3$ and ^{243}Am(thd)$_3$ chelates over a relatively low temperature range (100—150 °C).[7] This technique was found to be effective for a highly specific radioactive compound.

In the present study, the vapor pressure were determined as a function of temperature for 13 Ln(thd)$_3$ chelates by means of the Knudsen effusion technique, and their vacuum sublimation-recrystallizing temperatures were also determined by a sublimation apparatus with a continuous temperature gradient. Our purpose was to find what regularity might exist in the sublimation behavior. Some aspects of the sublimation behavior of Ln(thd)$_3$ chelates will be also discussed.

Experimental

Preparation of Ln(thd)$_3$ Chelates Labeled with Radioisotope. The purified lanthanoid oxides (99.9%) of La_2O_3, Pr_6O_{11}, Sm_2O_3, Eu_2O_3, Gd_2O_3, Tb_4O_7, Dy_2O_3, Ho_2O_3, Er_2O_3, Tm_2O_3, Lu_2O_3, and Y_2O_3 were each dissolved in a concentrated nitric acid solution. This was heated almost to dryness, then diluted with distilled water to make each stock solution. The gadolinium chloride of the radioisotope ^{153}Gd was purchased from The Radiochemical Centre (England). Other radioisotopes of ^{140}La, ^{142}Pr, ^{147}Nd, ^{153}Sm, ^{152}Eu, ^{160}Tb, ^{159}Dy, ^{166}Ho, ^{169}Er, ^{170}Tm, ^{169}Yb, and ^{177}Lu were produced from an (n,γ) nuclear reaction by irradiating each lanthanoid oxide with thermal neutrons in the reactor of Kyoto University. Yttrium radioisotope ^{88}Y was produced from a (γ,n) reaction by bremsstrahlung which was performed by using the LINAC of Tohoku University. Each radioisotope was dissolved in a minimum amount of concentrated nitric acid. Each radioisotope solution was added into the above stock solution of the same lanthanoid ion to make each solution be labeled with a radioisotope. The metal concentration and specific radioactivity of the solution were 10^{-2}—10^{-1} M and 10^{-3}—10^{2} μCi/μg of Ln, respectively.

The lanthanoid chelates, Ln(thd)$_3$, were prepared by the method of Eisentraut and Sievers[3] with a slight modification. The Ln nitrate solution (0.002 mol) labeled with radioisotopes was heated to dryness. The residue was dissolved in a minimum amount of 99% methanol, and pH of the resultant solution was adjusted between 3 and 5 by dropwise addition of 2 M NH_4OH solution. A solution of Hthd chelating agent (0.006 mol) in 10 ml of 99% methanol was then added to the above solution. The mixture was adjusted to the desired pH. The precipitate was filtered off, dried in a desiccator, then purified by recrystallization from chloroform and by two vacuum sublimations.

Vapor Pressure Measurements. Vapor pressures of the Ln(thd)$_3$ chelates were measured by a modified Knudsen effusion method. The major modifications from the normal Knudsen effusion method were as follows: (1) the Ln(thd)$_3$ chelate sublimated was collected stepwise at each temperature; (2) the amount of chelate on a collecting foil was determined by a radioactivity measurement. This method has the advantage that the spurous effluents caused by decomposition of the sample and/or volatile impurities have no corresponding lanthanoid metal and will not be counted. The relation between the amount of collected Ln(thd)$_3$ and the collecting time at a given temperature was linear beyond 5 min, as previously described in a preliminary work on the vapor pressure measurement of $Eu(thd)_3$ chelate.[7] The effusion rate of each $Ln(thd)_3$ chelate was determined from more than 4 weight-time data points at each temperature. For example, a series of measurements at the intervals of 5, 15, 8, and 10 min was carried out at the same temperature.

The Knudsen cell was made of 18-8 stainless steel, nearly cylindrical, 1.3 cm high, and 1.2 cm in diameter. Orifice parameters were photographed and measured on a microscope. An orifice with an area of 0.0021 cm^2 and a height of 0.032 cm was used.[8] The cell was attached to the bottom of a molecular still of the cold-finger type. The glass still with the above effusion cell was connected to a vacuum system. The pressure inside the vacuum line, as measured by a penning gauge, Daia Vacuum Engineering Model CT-2P, fell below 1×10^{-3} Torr (1 Torr=133.3224 Pa) within 30 s. The cell containing each $Ln(thd)_3$ chelate sample was heated by an oil bath, whose temperature was measured by a standard thermometer. The difference in temperature between the oil bath and the cell was calibrated by simultaneous measurement of the temperature of another cell within an enclosed thermometer in the same oil bath.

The effusion cell was loaded with 50 mg of sample, transported into the still, and evacuated to a vacuum of 1×10^{-5} Torr. The cell containing the sample chelate was exposed to the argon atomosphere. After the cell was heated for 1 h at a constant temperature in an argon atomosphere, it was evacuated. The effusion chelate gas collected on a water-cooled Al foil for more than 5 min. Effusing of the chelate gas was stopped by introducing argon into the vacuum line. The temperature of the oil bath and the collecting time of chelate gas were recorded. The collecting foil was replaced with a new aluminum foil.

The above procedure was repeated for a series of collecting intervals at a given temperature; the same repetitions were applied to various temperatures.

The collecting foil was dissolved in diluted hydrochloric acid. Radioactivity of each lanthanoid solution was measured by a NaI(Tl) scintillation counter, or by a Ge(Li) semiconductor detector. By using the specific radioactivity of the sample, the total weight of the collected chelate on the foil, W, was calculated. The rate of sublimation, m, is obtained by dividing the total weight of the collected chelate by the area of the orifice, the collecting time, and the Clausing factor: *i.e.* $m=W/atK$, where a is the area of the orifice, t is the collecting time, and K is the Clausing factor.[8]

Measurements of Vacuum Sublimation-recrystallizing Temperatures. A schematic drawing of the vacuum sublimation apparatus for the measurement of the vacuum sublimation-recrystallizing temperatures of the $Ln(thd)_3$ chelates is shown in Fig. 1. The apparatus has the advantage that the continuous temperature gradient along the sublimation tube can be obtained by sliding a electric furnace gently (1 °C/cm) or steeply (10 °C/cm) along the outer porcelain tube (5.8 cm in outer diameter and 166 cm in length), which consists of a copper tube (1.6 cm in outer diameter and 180 cm in length) covered with air and aluminum. The sublimation tube for introducing $Ln(thd)_3$ sample (10 mg) was evacuated to $1-10\times10^{-3}$ Torr, and placed in a definite position inside the sublimation apparatus. This had been heated and held at 180 °C before inserting the sublimation tube. The temperature gradients along the sublimation tube at various elapsed times are shown in Fig. 2. The sublimation of all $Ln(thd)_3$ chelates was carried out for 2 h under the above conditions. The radioactivity of the sublimate was scanned along the sublimation tube by sliding it on the lead slit of a NaI(Tl) scintillation detector. The highest temperature of the deposition zone on the wall of the sublimation tube was taken as a relative measure of the vacuum sublimation-recrystallizing temperature.

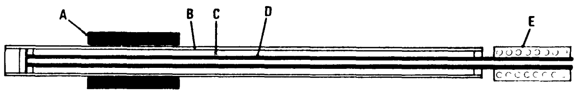

Fig. 1. Vacuum sublimation apparatus with continuous temperature gradient.
A: Electric furnace, B: outer porcelain tube, C: enclosed air and Al foil, D: copper tube, E: cooler.

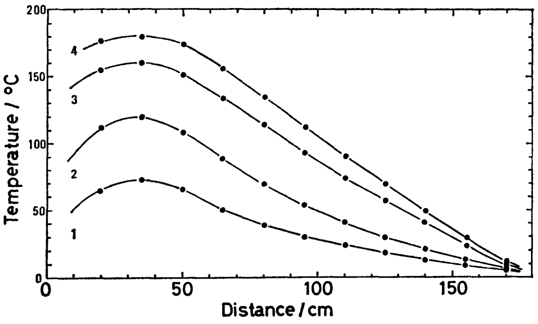

Fig. 2. Temperature gradient along vacuum sublimation tube at elapsed time.
1: 10 min, 2: 20 min, 3: 35 min, 4: 60—120 min.

IR and X-Ray Powder Diffraction Measurements. IR spectra of the $Ln(thd)_3$ chelates were obtained with a JASCO Model DS-701G spectrometer in the range of 4000 to 400 cm^{-1} by using the KBr pellet technique. X-Ray powder diffraction data were taken with nickel-filtered Cu $K\alpha$ radiation and recorded with a Rigaku Denki Diffractometer.

Results and Discussion

The rate of sublimation of each $Ln(thd)_3$ chelate was constant for collecting times longer than 5 min at a given temperature. Figure 3 shows that the relationship in the $Eu(thd)_3$ chelate between the weight of the collected chelate and the collecting time is linear at each temperature, and the slope of the straight lines is given as the apparent rate of sublimation of the Eu chelate. A slight amount of the collected chelate was easily measured by the radioactive tracer technique.[7] The rate of sublimation of each $Ln(thd)_3$ chelate was obtained over the temperature range of 100 to 150 °C

Vapor pressure, P, is calculated from the rate of sublimation, m, according to the following equation:[8]

$$P = m\{(2\pi RT)/M\}^{1/2}, \qquad (1)$$

where R is the gas constant; T, the absolute temperature of the sample; M, the molecular weight of the effusing gas. The units of m and P were chosen in g/(cm^2 s) and Torr, respectively (1 Torr=133.3224 Pa). The equation

$$P = 17.144\times m(T/M)^{1/2} \qquad (2)$$

is obtained. The vapor pressures of each $Ln(thd)_3$ chelate were fitted to the following equation:

$$\log P = -(\mathrm{A}/T) + \mathrm{B} \qquad (3)$$

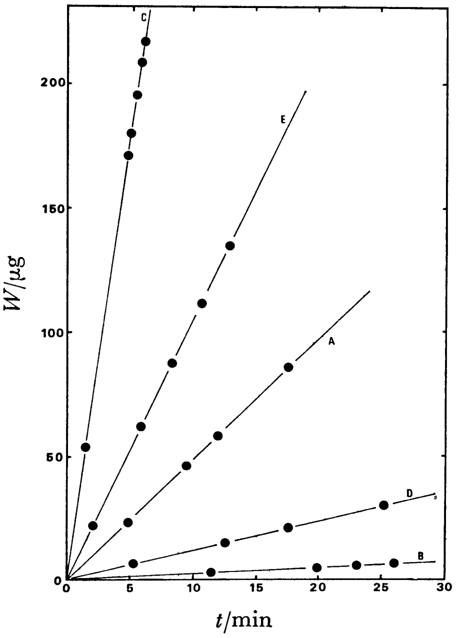

Fig. 3. Relation between amounts of collected Eu(thd)$_3$ chelate and collecting times at various temperatures.
A: 125.4 °C, B: 103.7 °C, C: 140.8 °C, D: 115.2 °C, E: 131.1 °C.

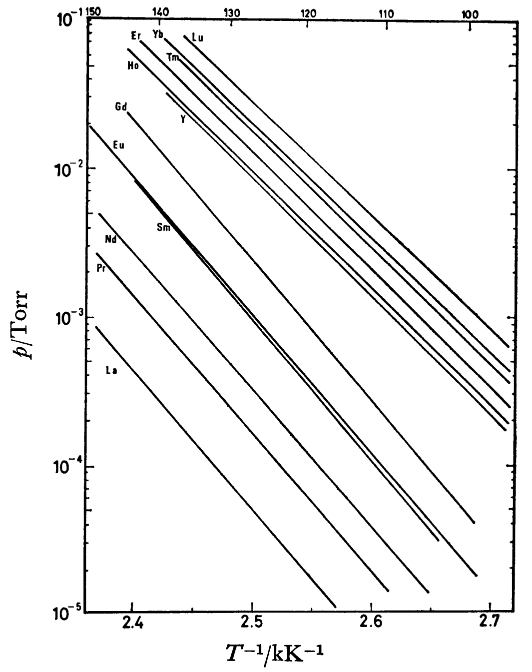

Fig. 4. Clausius-Clapeyron plots 11 Ln(thd)$_3$ and Y(thd)$_3$ chelates.

by a least square method. Heats of sublimation, ΔH_T, and entropies of sublimation, ΔS_T, were taken by equating the above experimental equation to the thermochemical equation

$$\ln(P/760) = (\Delta H_T - T\Delta S_T)/(-RT). \qquad (4)$$

Thus, $\Delta H_T = 2.303 \times AR$ and $\Delta S_T = 2.303 \times R$(B-log 760) were obtained.

The Clausius-Clapeyron plots of a series of Ln(thd)$_3$ (expect Tb(thd)$_3$ and Dy(thd)$_3$) and Y(thd)$_3$ chelates are shown and compared in Fig. 4. Table 1 summarizes the thermochemical constants obtained. The plots of the Tb and Dy chelates were found to break at definite temperatures. The vapor pressures of these two chelates were measured in more detail in the temperature-descending process (160→100 °C), and the temperature-ascending process (100→160 °C). Figure 5 shows the Clausius-Clapeyron plots obtained in both processes for these chelates. Table 2 gives their thermochemical constants. The vapor pressures of the Ln(thd)$_3$ chelates have been found to increase with atomic number of lanthanoid ion, according to Sicre *et al.*[4] Figure 4 shows the same phenomena. The enthalpies of sublimation of the chelates of La to Gd, and Ho to Lu are slightly different from those of Sicre *et al.*

However, the Clausius-Clapeyron plots obtained in the temperature-ascending process of the Tb(thd)$_3$ chelate were found to break at 147 °C, where the crystal structure of this chelate changed thermally

TABLE 1. VAPOR PRESSURES AND ENTHALPIES OF SUBLIMATION OF LANTHANOID AND Y CHELATES

(1 cal=4.184 J)

Sample	A$^{a)}$	B$^{a)}$	Error %	Limit °C	ΔH_T° kcal mol^{-1}	ΔS_T° cal K^{-1} mol^{-1}
La$_2$(thd)$_6$	9382.7	19.149	4	115—150	42.9	74.4
Pr$_2$(thd)$_6$	9333.5	19.553	3	110—150	42.7	76.3
Nd$_2$(thd)$_6$	9248.1	19.622	3	105—150	42.3	76.6
Sm$_2$(thd)$_6$	9440.4	20.573	3	105—145	43.2	81.0
Eu$_2$(thd)$_6$	9400.3	20.496	2	90—160	43.0	80.6
Gd$_2$(thd)$_6$	9242.4	20.468	3	100—145	43.3	80.5
Ho(thd)$_3$	7978.1	17.917	2	90—145	36.5	68.8
Er(thd)$_3$	8041.0	18.202	3	90—145	36.8	70.1
Tm(thd)$_3$	8159.3	18.650	3	90—140	37.3	72.2
Yb(thd)$_3$	8145.9	18.677	3	90—145	37.3	72.3
Lu(thd)$_3$	8085.2	18.672	3	90—140	37.0	72.3
Y(thd)$_3$	8211.7	18.463	2	90—140	37.5	71.3

a) Log P(Torr) = −(A/T)+B.

TABLE 2. VAPOR PRESSURES AND ENTHALPIES OF SUBLIMATION OF Tb AND Dy CHELATES

(1 cal=4.184 J)

Sample	A[a)]	B[a)]	Error %	Limit °C	ΔH°_T kcal mol^{-1}	ΔS°_T cal K^{-1} mol^{-1}
$Tb_2(thd)_6$	9072.6	20.238	3	100—147	41.5	79.4
$Tb(thd)_3$	7897.3	17.464	3	100—160	36.1	66.7
$Dy_2(thd)_6$	8963.8	20.390	6	100—115	41.0	80.1
$Dy(thd)_3$	7934.2	17.627	3	100—140	36.3	67.5

a) $\log P(\text{Torr}) = -(A/T) + B$.

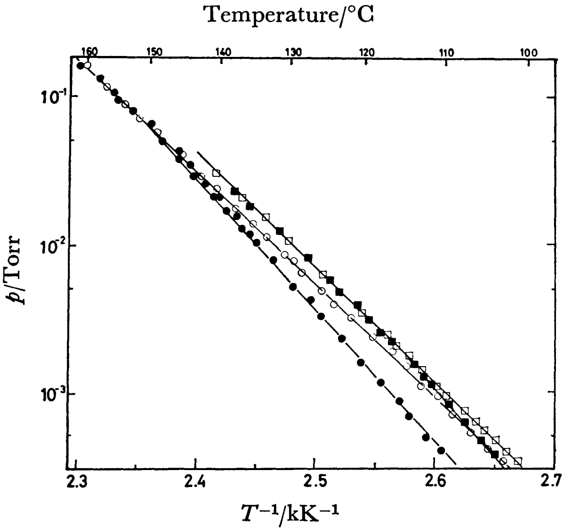

Fig. 5. Clausius-Clapeyron plots of $Tb(thd)_3$ and $Dy(thd)_3$ chelates.
●: Temperature-ascending process of the Tb chelate,
○: temperature-descending process of the Tb chelate,
■: temperature-ascending process of the Dy chelate,
□: temperature-descending process of the Dy chelate.

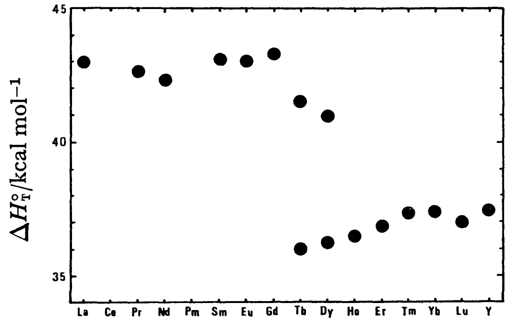

Fig. 6. Enthalpies of sublimation of $Ln(thd)_3$ as a function of atomic number.

from a monoclinic dimer to an orthorhombic monomer.[9)] The enthalpy of sublimation of the Tb chelate in lower temperature range (100—147 °C) was similar to those of lighter lanthanoids (La to Gd), and the enthalpy in upper temperature range (147—160 °C) resembled those of heavier lanthanoids (Ho to Lu) and yttrium. On the other hand, the Clausius-Clapeyron plots in the temperature-descending processess did not break at 147 °C and followed a straight line. The enthalpy of sublimation obtained from this line was the same as those in the upper temperature range (147—160 °C) of the ascending process, and almost equal to those of heavier lanthanoid chelates. The sublimation behavior of $Dy(thd)_3$ chelate is similar to that of the Tb chelate. The Dy chelate also changed its crystal structure at about 115 °C. The thermal transitions of the Tb and Dy chelates were found to be irreversible. The thermal behaviors of the $Ln(thd)_3$ chelates were found to be classified into three groups: La to Gd, Tb and Dy, and Ho to Lu. Figure 6 gives a relationship between the enthalpy of sublimation and the atomic number. The difference in enthalpy of sublimation between the lighter lanthanoids (La to Gd) and the heavier ones (Ho to Lu) is 6—8 kcal/mol (1 cal=4.184 J), which appears to correspond to the transition enthalpy of dimer to monomer of the Tb and Dy chelates.

Partial X-ray powder patterns of the $Ln(thd)_3$ chelates are compared in Table 3. The patterns of the lighter lanthanoid chelates of La to Gd were different from those of heavier ones of Ho to Lu and yttrium. Erasmus and Boeyens reported the Pr chelate to be a monoclinic dimer.[10)] The crystal structure of $Er(thd)_3$ and $Lu(thd)_3$ chelates have also been reported to be those of an orthorhombic monomer.[11,12)] The crystal structure of the Tb chelate is the same as those of the lighter lanthanoid chelates. In the previous work,[9)] the freshly sublimated Tb chelate has been found to change in crystallographic modification from a monoclinic dimer to an orthorhombic monomer at 147 °C, by means of differential scanning calorimetric technique and X-ray powder diffraction at elevated temperature. The breaking point on the Clausius-Clapeyron line of the Tb chelate corresponds to the temperature of its thermal transition. Fresh $Dy(thd)_3$ chelate was obtained in two different X-ray crystallographic systems by vacuum sublimation: a monoclinic dimer form and an orthorhombic monomer form. Vapor of the Dy chelate crystallizes in orthorhombic monomer form under the sublimation condition with a gentle temperature gradient, although it deposits in the monoclinic dimer form on the cooler of the molecular still if sublimed with a steep temperature gradient (100 °C/cm). Infra-red spectra of the freshly prepared lighter lanthanoid chelates were different from those of the heavier ones at 1300—1250 cm^{-1}, 1250—1100 cm^{-1}, 970—940 cm^{-1}, 810—770 cm^{-1}, and 510—450 cm^{-1}, as shown in Fig. 7. The spectral shape of the fresh Tb chelate was compared with those of lighter lanthanoid (La, Pr-Gd) chelates and found to be identical over the range of 4000 to 600 cm^{-1}. On the other hand, the IR spectra

TABLE 3. PARTIAL X-RAY POWDER PATTERNS OF SOME LANTHANOID AND Y CHELATES (d, Å)

$La_2(thd)_6$	$Pr_2(thd)_6$	$Nd_2(thd)_6$	$Eu_2(thd)_6$	$Gd_2(thd)_6$	$Tb_2(thd)_6$	$Dy(thd)_3$	$Ho(thd)_3$	$Er(thd)_3$	$Yb(thd)_3$	$Y(thd)_3$
14.72 w	14.48 w	14.48 w	14.48 w	14.48 w	14.48 w					
13.59 w		13.59 w								
12.22 s	11.94 s	12.02 s	11.94 s	12.05 s	11.94 s					
11.40 s	11.25 m	11.32 s	11.32 s	11.32 s	11.18 s					
10.84 s	10.84 s	10.84 s	10.91 s	10.91 s	10.91 s					
						10.84 s	10.80 s	10.79 s	10.77 s	10.77 s
	10.21 w		10.16 w	10.21 w	10.10 w					
9.66 m	9.60 w		9.60 w	9.66 m	9.60 w					
9.11 w	9.20 w	9.30 w	9.30 w	9.28 m	9.20 m	9.30 s	9.28 s	9.30 s	9.20 s	9.25 s
							9.06 m	9.06 m	9.06 m	9.06 m
8.88 w	8.93 m	8.93 m	8.93 m	8.93 m	8.88 m					
						8.84 m	8.84 s	8.84 s	8.79 s	8.84 s
						7.37 m	7.37 m	7.37 m	7.34 m	7.37 m
						6.91 m	6.91 m	6.91 s	6.86 s	6.91 m
						6.80 m	6.80 m	6.83 m	6.80 m	6.80 m
	5.69 w	5.71 w	5.71 w	5.73 w	5.71 w	5.68 w	5.69 w	5.71 w	5.64 w	5.68 w
	5.38 w	5.37 w	5.35 w	5.37 w	5.34 w	5.37 w	5.35 w	5.34 w	5.34 w	5.34 w
						5.17 s	5.15 s	5.15 s	5.11 s	5.15 s
	5.00 w	5.00 w	5.00 w	5.00 w	4.98 w	5.00 m	5.03 m	5.03 m	5.00 m	5.02 m
4.75 w	4.74 w					4.71 m	4.72 m	4.72 m	4.71 m	4.72 m
4.67 w	4.67 m	4.67 m	4.65 m	4.67 m	4.64 m	4.64 m	4.64 m	4.64 m	4.61 m	4.64 m
4.62 w	4.62 m	4.59 m	4.58 m	4.59 m	4.57 m	4.55 s	4.55 m	4.58 m	4.55 m	4.57 m
							4.50 w	4.50 w	4.46 w	4.49 w
						4.39 m	4.39 s	4.39 s	4.39 s	4.40 s
		4.32 w	4.31 w	4.31 w	4.27 w					
		4.20 w	4.22 w	4.19 w	4.21 w	4.17 m	4.18 m	4.21 m	4.16 m	4.18 m
						4.05 m	4.05 m	4.05 w	4.04 m	4.05 m

s = Strong; m = medium; w = weak.

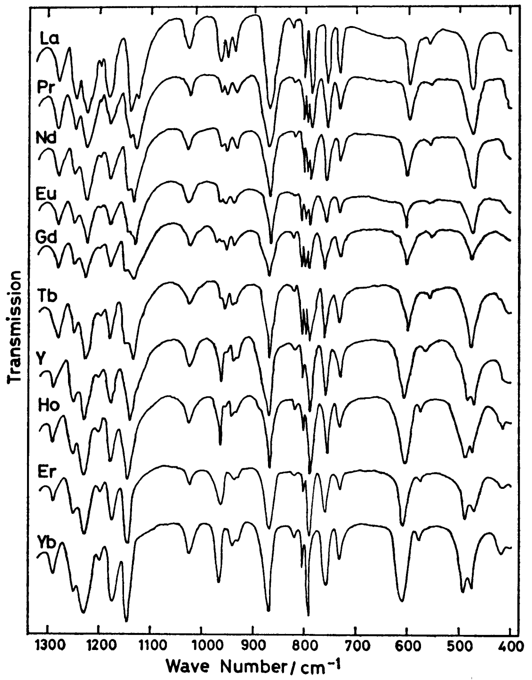

Fig. 7. IR spectra of the freshly sublimated $Ln(thd)_3$ and $Y(thd)_3$ chelates.

of the pre-heated Tb and Dy chelates were identical with those of the heavier lanthanoid (Ho–Lu) chelates.

TABLE 4. VACUUM SUBLIMATION-RECRYSTALLIZING TEMPERATURE RANGES OF LANTHANOID AND Y CHELATES

Sample	Temperature range/°C
$La_2(thd)_6$	88—141
$Pr_2(thd)_6$	88—139
$Nd_2(thd)_6$	86—137
$Sm_2(thd)_6$	87—129
$Eu_2(thd)_6$	79—126
$Gd_2(thd)_6$	74—125
$Tb_2(thd)_6$	66—117
$Dy(thd)_3$	46—75
$Ho(thd)_3$	49—74
$Er(thd)_3$	49—74
$Tm(thd)_3$	48—71
$Yb(thd)_3$	45—66
$Lu(thd)_3$	46—67
$Y(thd)_3$	52—80

Vacuum sublimation-recrystallizing temperature zones can be observed discretely and reproducibly at the higher temperature site of the deposition zone, while the tailing appears in its lower temperature site. The vacuum sublimation-recrystallizing temperature zones of the $Ln(thd)_3$ chelates are summarized in Table 4. Figure 8 shows the plots of the highest temperature of vacuum sublimation-recrystallizing zone

Table 5. Critical values of lanthanoid and Y chelates

Sample	$P_{180\,°C}$ a)	$P_{v.s.r.}$ b)	γ c)
$La_2(thd)_6$	2.7×10^{-2}	3.0×10^{-4}	9.0×10^{1}
$Pr_2(thd)_6$	8.9×10^{-2}	7.9×10^{-4}	1.1×10^{2}
$Nd_2(thd)_6$	1.6×10^{-1}	1.2×10^{-3}	1.3×10^{2}
$Sm_2(thd)_6$	5.4×10^{-1}	1.2×10^{-3}	4.5×10^{2}
$Eu_2(thd)_6$	5.6×10^{-1}	8.6×10^{-4}	6.5×10^{2}
$Gd_2(thd)_6$	1.2	1.8×10^{-3}	6.7×10^{2}
$Tb_2(thd)_6$	1.1	1.6×10^{-3}	6.9×10^{2}
$Dy(thd)_3$	1.3	6.7×10^{-6}	1.9×10^{5}
$Ho(thd)_3$	2.0	8.4×10^{-6}	2.4×10^{5}
$Er(thd)_3$	2.8	1.1×10^{-5}	2.5×10^{5}
$Tm(thd)_3$	4.4	8.5×10^{-6}	5.2×10^{5}
$Yb(thd)_3$	5.0	4.4×10^{-6}	1.1×10^{6}
$Lu(thd)_3$	6.7	7.8×10^{-6}	8.6×10^{5}
$Y(thd)_3$	2.2	1.6×10^{-5}	1.4×10^{6}

a) $P_{180\,°C}$ indicates the pressure of chelate gas which is taken as the vapor pressure of the chelate at the temperature of heating site(180 °C). b) $P_{v.s.r.}$ is the saturated vapor pressure of the chelate at the highest site of vacuum sublimation-recrystallizing temperature. c) γ is the critical value calculated from the equation, $\gamma = P_{180\,°C}/P_{v.s.r.}$.

as a function of the atomic number of the corresponding lanthanoid. The plots can be classified in two distinct groups (La to Tb, and Dy to Lu) that coincided with the two different crystal structures observed from X-ray powder diffraction patterns. The $Dy(thd)_3$ chelate purified under the gentle temperature gradient belonged to a class of heavier lanthanoids. The lighter lanthanoids (La to Tb) form a monoclinic dimer system, and heavier ones (Dy to Lu) recrystallize in orthorhombic form on purification from the vapor phase. The vacuum sublimation-recrystallizing temperature can be explained on the basis of crystallization in the dimeric or monomeric system from the chelate vapor. Monomeric chelate gas of the lanthanoid will solidify to form a dimer system according to either of the following equations:

$$2Ln(thd)_3(gas) \rightarrow Ln_2(thd)_6(gas) \rightarrow Ln_2(thd)_6(solid), \tag{5}$$

or

$$2Ln(thd)_3(gas) \rightarrow 2Ln(thd)_3(solid) \rightarrow Ln_2(thd)_6(solid). \tag{6}$$

The enthalpies of the above two reactions are larger than that of the reaction of monomeric gas to monomeric solid. The enthalpy of sublimation of a monomeric $Ln(thd)_3(solid)$ nearly equals 36 kcal/mol, and that of dimeric chelate is about 43 kcal/mol. From these results, the difference in the enthalpy of sublimation corresponds to the transition enthalpy of the following reaction:

$$Ln_2(thd)_6(soid) \rightarrow 2Ln(thd)_3(solid), \tag{7}$$

where the transition enthalpy of the reaction nearly equals 7 kcal/mol. In fact, the dimeric Tb and Dy chelates change to the monomeric chelates endothermically.[9] The enthalpies of both processes of (6) can be calculated from the thermochemical data obtained in this experiment. The volatilization process of the lighter lanthanoid chelate, $Ln_2(thd)_6$, is represented by the reverse of reaction (5) or (6). The lighter chelate thus requires more energy to vaporize than the heavier one. Deposition temperature is derived from overall sublimation-recrystallization processes. The lighter chelate deposits in a higher temperature zone than the heavier one. In general, the growth of crystals can be definitely observed at the "critical temperature."[13] Moreover, the ratio $\gamma = P_h/P_c$, where P_h is the pressure of vapor phase and P_c is the saturated vapor pressure at the critical temperature, have a characteristic value for each sample; this value is called the "critical value."[13] The vacuum sublimation-recrystallizing temperature in this paper corresponds to the critical temperature. The critical values have been calculated to the individual lanthanoid chelates to find out what regularity may exist in vacuum sublimation-recrystallization behavior; their values are given in Table 5. The critical values of the lanthanoid chelates were classified into two groups (La to Tb, and Dy to Lu) that coincided with the groupings of the vacuum sublimation-recrystallizing temperature. To estimate vacuum sublimation-recrystallizing temperatures of a variety of β-diketonato chelates, it would be necessary to collect the data of vapor pressures over the temperature range of deposition zone and critical values for these compounds.

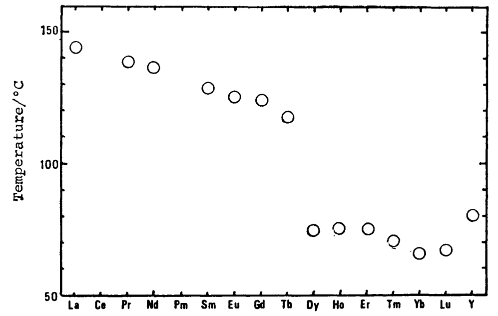

Fig. 8. Vacuum sublimation-recrystallizing temperatures of $Ln(thd)_3$ as a function of atomic number.

The authors wish to express their thanks to Professor Eishin Kyuno of Hokuriku University for his kind permission to use the IR instruments. The present work was partially supported by a Grant-in-Aid for Scientific Research No. 374189 and No. 574227 from the Ministry of Education, Science and Culture.

References

1) R. E. Sievers and J. E. Sadlowski, *Science*, **201**, 217 (1980); W. F. Libby, *ibid.*, **171**, 499 (1971); L. A. Pedersen and W. F. Libby, *ibid.*, **176**, 1355 (1972); R. C. Vickery, *ibid.*, **172**, 86 (1971); R. J. H. Voorhoeve, J. P. Remeika, P. E. Freeland, and B. T. Matthias, *ibid.*, **177**, 353 (1972).

2) R. L. Van Hemert, L. B. Spendlove, and R. E. Sievers, *J. Electrochem. Soc.*, **112**, 1123 (1965); S. C. Chattoraj, A. G. Cupka, Jr., and R. E. Sievers, *J. Inorg. Nucl. Chem.*, **28**, 1937 (1966).

3) K. J. Eisentraut and R. E. Sievers, *J. Am. Chem. Soc.*, **87**, 5254 (1965).

4) J. E. Sicre, J. T. Dubois, K. J. Eisentraut, and R. E. Sievers, *J. Am. Chem. Soc.*, **91**, 3476 (1969).

5) E. W. Berg and J. J. C. Acosta, *Anal. Chim. Acta*, **40**, 101 (1968).

6) M. Sakanoue and R. Amano, "Transplutonium 1975," ed by W. Müller and R. Lindner, North-Holland Publ. Co., (1976), p. 123.

7) R. Amano, A. Sato, and S. Suzuki, *Radiochem. Radioanal. Lett.*, **39**, 441 (1979).

8) P. Clausing, *Ann. Phys.*, **12**, 961 (1932); S. Saito and M. Kinoshita, "Jiken-kagaku-kōza, Zoku-2, Bunri-to-seisei," Maruzen, Tokyo (1967), p. 69; T. Sata, "Shin-jiken-kagaku-kōza, 2, Netsu-atsuryoku," Maruzen, Tokyo (1977), p. 371.

9) R. Amano, A. Sato, and S. Suzuki, *Chem. Lett.*, **1980**, 537.

10) C. S. Erasmus and J. C. A. Boeyens, *Acta Crystallogr., Sect. B*, **26**, 1843 (1970).

11) J. P. R. Villiers and J. C. A. Boeyens, *Acta Crystallogr., Sect. B*, **28**, 2335 (1972).

12) S. Onuma, H. Inoue, and S. Shibata, *Bull. Chem. Soc. Jpn.*, **49**, 644 (1976).

13) M. Knudsen, *Ann. Phys.*, **50**, 472 (1916); R. W. Wood, *Phil. Mag.*, **32**, 364 (1916); K. Yoshimura, *Jpn. Anal.*, **11**, 397, 400 (1962).