CHEMISTRY LETTERS, pp. 537-540, 1980.

THERMAL TRANSITION OF DIMERIC TRIS(2,2,6,6-TETRAMETHYL-3,5-HEPTANEDIONATO)TERBIUM(III)

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The crystal structure of the title compound was found to change thermally from a monoclinic dimer to an orthorhombic monomer at 147 °C. The transition enthalpy and temperature were determined from differential scanning calorimetric measurements.

The lanthanoid(III) chelates with 2,2,6,6-tetramethyl-3,5-heptanedione(Hthd) have been known to exist in two different crystallographic modifications with the change occurring at dysprosium.[1-4] Lighter lanthanoids, La to Dy, form monoclinic dimer chelates, $Ln_2(thd)_6$, and heavier ones, Ho to Lu, crystallize in an orthorhombic monomer form, $Ln(thd)_3$, on purification from the vapor phase.[2,3]

In this work, the thermal behavior of the terbium(III) chelate was examined over the temperature range 30 to 190 °C by differential scanning calorimetry(DSC), X-ray powder diffraction and IR measurements, and compared with those of the Pr, Eu, Er, and Yb chelates.

The $Ln(thd)_3$ (Ln=Pr, Eu, Tb, Er, Yb) samples were prepared after the well established procedure,[5] and purified at least twice by vacuum sublimation with temperature gradient from 180 °C to room temperature. The lanthanoid chelates were deposited at their characteristic temperature points of 120 to 70 °C with increasing order of atomic number.[6] The purity and composition of the freshly sublimated samples were examined by melting point and C, H and metal analysis. The results were in agreement with literature data.[5] The transition enthalpies and temperatures were measured by using a Rigaku-Denki Model DSC-8055 differential scanning calorimeter. The measurement was performed on about 10 mg of sample packed in aluminum can at a heating rate of 1.25 °C/min or 10 °C/min. Indium metal(99.999%) was used as the standard. X-ray powder patterns were taken at different temperatures up to 155 °C with a diffractometer using nickel filtered Cu-Kα radiation. Temperatures were measured by a thermocouple embedded together with heating element in sample holding plate of copper. IR measurement was performed over the range of 4000-400 cm^{-1} by using of KBr pellet technique.

The X-ray powder patterns of the Pr, Eu, Tb, Er, and Yb chelates obtained at room temperature are compared in Table 1 (A). It is found that the crystal structure of the Tb chelate is the same as those of the Pr and Eu chelates, but different from those of the Er and Yb chelates. None of these patterns changes at the temperature up to 100 °C. Erasmus and Boeyens reported the Pr chelate to be a monoclinic dimer form.[2] The present result indicates that the freshly sublimated Tb chelate is of the same crystal form as that of the Pr chelate. In Table 1 (B), the X-ray powder patterns of the Tb chelate at 100, 130, 140, and 155 °C are given. The X-ray pattern at 155 °C is the same as those of the Er and Yb chelates. The crystal structures of the Er and Lu chelates have been reported to be as an orthorhombic monomer.[3,4] It is suggested from these facts that the crystal structure of the Tb chelate changes thermally to an orthorhombic monomer. X-ray powder pattern of the Tb chelate preheated at 155 °C was also quite similar to those of the Er and Yb chelates. From these results the thermal trasition of the fresh Tb chelate occurred as follows:

$$\underset{\text{monoclinic}}{\mathrm{Tb_2(thd)_6}} \longrightarrow \underset{\text{orthorhombic}}{\mathrm{2\ Tb(thd)_3}}\ .$$

X-ray powder patterns of the Pr, Eu, Er and Yb chelates did not change over temperature range 20 to 155 °C.

Infrared spectrum of the freshly prepared Tb chelate was different from that of the

Table 1. Partial X-ray Powder Patterns (d,Å)

(A). Data for Some Lanthanoid Chelates at Room Temperature.					(B). Data for The Tb Chelate at Various Temperatures.			
$Pr_2(thd)_6$	$Eu_2(thd)_6$	$Tb_2(thd)_6$	$Er(thd)_3$	$Yb(thd)_3$	100°C	130°C	140°C	155°C
14.48w	14.48w	14.48w			14.48w			
11.94s	11.94s	11.94s			11.94s	11.88m	11.62s	
11.25m	11.32s	11.18s			11.05s	11.04s	11.04m	
10.84s	10.91s	11.91s			11.84s			
			10.79s	10.77s				10.80s
10.21w	10.16w	10.10w						
9.60w	9.60w	9.60w			9.60w			
9.20w	9.30w	9.20w	9.30s	9.20s	9.20w		9.11m	9.30s
			9.06m	9.06w				
8.93m	8.93m	8.88m			8.90m	8.92m		
			8.84s	8.79s				8.84s
			7.37m	7.34m			7.56m	7.35m
			6.91m	6.86s			6.96m	6.96m
			6.83m	6.80m				6.80m
5.69w	5.71w	5.71w	5.71w	5.64w	5.74w	5.79w		
5.38w	5.35w	5.34w	5.34w	5.34w			5.30m	5.36w
			5.15s	5.11s			5.18m	5.15s
5.00w	5.00w	4.98w	5.03m	5.00m	5.04w	5.04w		5.01w
4.74w			4.72m	4.71m			4.70w	
4.67m	4.65m	4.64m	4.64m	4.61m	4.64m	4.69m	4.66w	4.65m
4.62m	4.58m	4.57m	4.58w	4.55m	4.57m	4.61m	4.58w	4.56m
			4.50w	4.46w			4.54m	
			4.39s	4.39s				4.39s
	4.31w	4.27w			4.34w	4.32w		
	4.20w	4.21w	4.21w	4.16m			4.20m	4.17m
			4.05w	4.04m			4.07m	4.05w

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

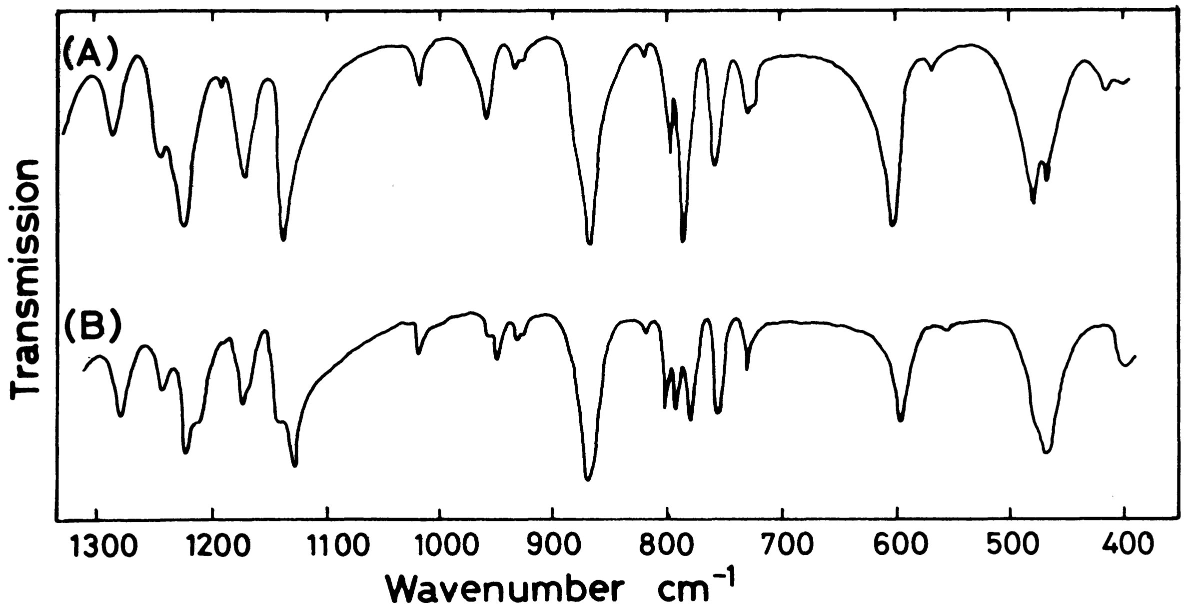

Fig. 1. IR Spectra of The Tb Chelate (A) Preheated (B) Freshly Prepared.

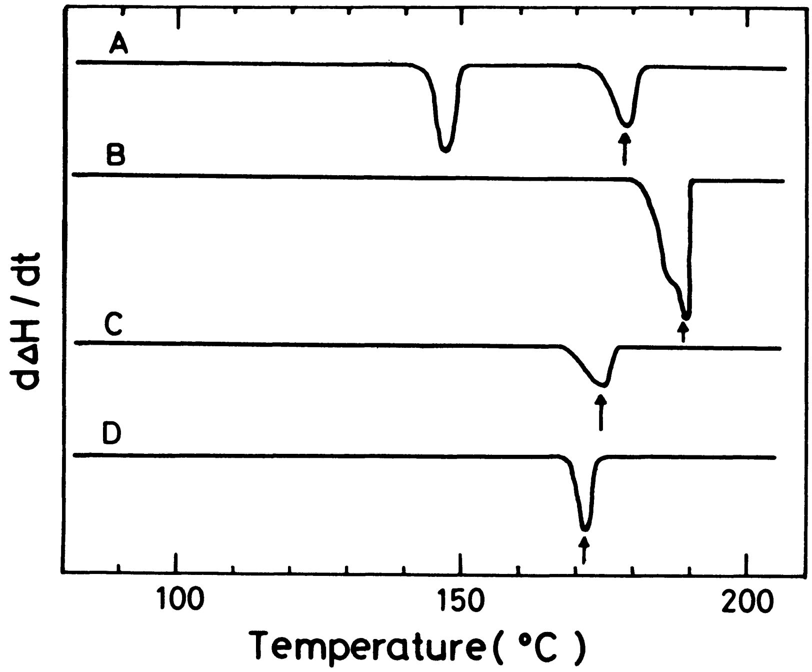

Fig. 2. DSC Curves for Some Lanthanoid thd Chelates. (A) $Tb_2(thd)_6$, (B) $Eu_2(thd)_6$, (C) $Er(thd)_3$, (D) $Yb(thd)_3$. Arrows indicate melting temperature.

preheated one at 1300-1250 cm^{-1}, 1250-1100cm^{-1}, 970-940cm^{-1}, 810-770cm^{-1}, and 510-450 cm^{-1}. The spectral shapes of the lighter lanthanoids (La, Pr-Gd) were compared with that of the fresh Tb chelate and found all to be identical over 4000-600 cm^{-1}. On the other hand, the IR spectrum of the preheated chelate was identical with those of the heavier lanthanoids(Ho to Lu).

The DSC curves of some lanthanoid chelates are given in Fig. 2. The curve A is for the fresh Tb chelate. The trasition of $Tb_2(thd)_6$ to $Tb(thd)_3$ is shown to occur at 147 °C endothermically, and $Tb(thd)_3$ melts at 179.5 °C. In cooling from 160 to 30 °C, the DSC curve of the Tb sample showed no change in $d\Delta H/dt$, suggesting that the transition of the monoclinic dimer to the orthorhombic monomer is irreversible. The curve B,C and D in Fig. 2 are of the Eu, Er and Yb chelates, respectively, which show that these compounds melt without transition.

Table 2. Enthalpies and Temperatures of Transition and Melting for The Tb, Eu, Er and Yb Chelates with thd Ligand. 1cal= 4.184J

Reaction	Temperature(°C)	$\Delta H°$(kcal/mol)
$Tb_2(thd)_6$ $2Tb(thd)_3$	147	6.2(per mole of $Tb(thd)_3$)
$Tb(thd)_3$ melting	179.5	5.9
$Eu_2(thd)_6$ melting	189	12.0(per mole of $Eu(thd)_3$)
$Er(thd)_3$ melting	175	11.6
$Yb(thd)_3$ melting	171.5	12.1

The enthalpies and temperatures of transition and melting determined from the DSC curves are listed in Table 2. The sum of the enthalpy changes of the transition and melting for the fresh $Tb_2(thd)_6$ were nearly equal to those of $Eu_2(thd)_6$, $Er(thd)_3$ and $Yb(thd)_3$.

The present results lead a simple preparation of two crystalline form of the Tb thd chelate, monoclinic dimer and orthorhombic monomer, and offers a possible comparative study on physicochemical properties of these compounds.

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(Received March 3, 1980)