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LETTER

A volatile thallium chelate, (2,2,6,6-tetramethyl-3,5-heptanedionato)Tl(I)

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Volatile metal chelates have been used in a wide range of applications as fuel additives and catalysts, as metal vapor sources, and in trace metal analysis [1]. There is growing interest in volatile metal β-diketone chelates as vapor source for chemical vapor deposition (CVD). We have been interested in CVD using the volatile β-diketone chelates with 2,2,6,6,-tetramethyl-3,5-heptanedione (thd), and developed the new preparation method of metal oxide, sulfide and fluoride films [2–5]. On the other hand, thallium is known to be a key component of a variety of optical and superconducting materials [6, 7]. Some volatile and stable thallium chelates are required as its vapor source for CVD. We here describe some characteristics of (2,2,6,6,-tetramethyl-3,5-heptanedionato)thallium(I), hereafter abbreviated as Tl(thd), and preliminary experiments in the CVD between this chelate and some reactant gases.

Tl(thd) was prepared as follows. The chelating agent H(thd) was added to ethanolic thallium(I) solution, and the pH value of the resultant solution was then adjusted to 9–10 by adding diluted NaOH solution. The precipitation was isolated by filtration, allowed to dry, and was purified by sublimation in vacuum. The purified Tl(thd), m.p. 173 °C, was yellowish-green crystalline, stable and non-hygroscopic. *Anal.* Calc. for $TlC_{11}H_{19}O_2$: C, 34.08; H, 4.94. Found: C, 33.54; H, 4.91%. Furthermore, the characterization of the Tl chelate was performed by the use of IR and mass spectrometries, and thermogravimetric analysis.

Table 1 lists the several peaks observed in the mass spectrum of Tl(thd) along with their tentative assignments and intensities. In addition to the expected $Tl(thd)^+$ peak, the species corresponding to $C(CH_3)_3{}^+$, $COCHCOC(CH_3)_3{}^+$, $H(thd)^+$, Tl^+ and $Tl(COCHCOC(CH_3)_3)^+$ were mainly observed. Five very weak peaks were also found at mass 422, 525, 548, 593 and 605 in the higher mass region. The two peaks at 548 and 593 can be assigned to $Tl_2(CH_3CCOCHCOC(CH_3)_2)^+$ and $Tl_2(thd)^+$, respectively. However, these higher-mass peaks could not be observed with a temperature lower than 110 °C and higher than 170 °C. Figure 1 compares the thermogram of the Tl(thd) chelate with those of the $Nd_2(thd)_6$ and $Yb(thd)_3$ chelates, whose volatilities have been well established [8, 9], and gives us the preliminary information as a thallium vapor source for our CVD experiment. The Tl(thd) chelate appeared to be more volatile than a series of lanthanide thd chelates.

TABLE 1. Partial list of peaks in the mass spectrum of Tl(thd)

Mass number	Assignment[a]	Intensity[b]
605	N.A.	vvw
593	$Tl_2(thd)^+$	vvw
548	$Tl_2(CH_3CCOCHCOC(CH_3)_2)^+$	vvw
525	N.A.	vvw
422	N.A.	vw
388	$Tl(thd)^+$	m
331	$Tl(COCHCOC(CH_3)_3)^+$	s
205	Tl^+	vs
184	$H(thd)^+$	s
127	$COCHCOC(CH_3)_3{}^+$	s
57	$C(CH_3)_3{}^+$	s

[a]N.A. = not assigned. [b]s = strong, m = medium, w = weak, v = very.

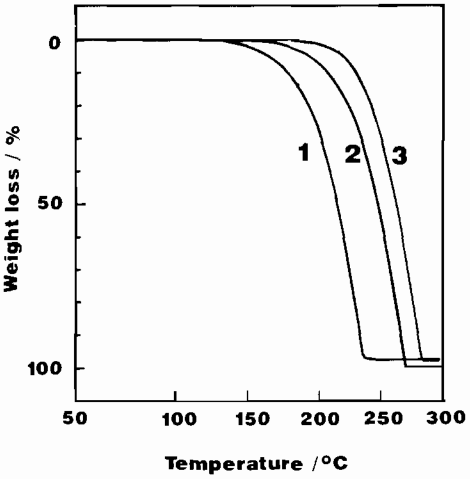

Fig. 1. Thermograms of thallium, ytterbium and neodymium chelates with 2,2,6,6,-tetramethyl-3,5-heptanedione. 1: Tl(thd); 2: $Yb(thd)_3$; 3: $Nd_2(thd)_6$.

From the above results, we believe that Tl(thd) is a 1:1 complex between Tl metal and the thd ligand,

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and a thallium atom is bonded to the two oxygen atoms of one ligand to make chelation, and moreover each 1:1 thallium–thd unit is linked to neighboring thd molecules to form a polymeric structure. No dimeric $Tl_2(thd)_2^+$ ($m/e=776$) peak in the mass spectrum is directly observed, but metastable peaks can be observed corresponding to the processes:

$$Tl_2(thd)_2^+ \longrightarrow Tl_2(thd)^+ \ (m/e=593)+\mathrm{thd}$$

$$Tl_2(thd)^+ \longrightarrow Tl_2(CH_3CCOCHCOC(CH_3)_2)^+ \ (m/e=548)+3CH_3$$

This may explain that the Tl chelate is partly dimeric in the vapor phase and the possible dimeric species will be too short-lived to be recorded, as described in an earlier report on Tl(acac) [10], but it is difficult to confirm it without further detailed experiments. Anyway, the Tl(thd) chelate was found to be the most volatile and stable among Tl β-diketone chelates, although Tl(acac) had been used as a vapor source [11].

Next, we examined the CVD using the Tl(thd) chelate to confirm its versatility as a vapor precursor. Thallium chloride and bromide were prepared in the CVD system using CF_2Cl_2/O_2 and CF_3Br/O_2 gas mixtures, respectively. The depositions were carried out in a horizontal hot-wall type apparatus, which consisted of two neighboring zones (vaporization and reaction zones), as described elsewhere [2]. The Tl(thd) source chelate was placed in the vaporization zone with a temperature of 180 °C and the CVD was initiated in the reaction zone at a temperature of 450 °C. The flow rates of carrier and reactant gases were controlled at 50 ml/min. The as-grown products were examined by X-ray diffraction. As a result, the lattice constants of TlCl and TlBr obtained in these CVD experiments are summarized in Table 2. These values are in close agreement with the published values [12, 13].

TABLE 2. Lattice constants of TlCl[a] and TlBr[a]

	This work	Literature data
TlCl	3.84(1) Å[b]	3.8421 Å[c]
TlBr	3.98(4) Å[b]	3.9850 Å[d]

[a]Crystal system: cubic; space group *Pm3m*. [b]Cu Kα, $\lambda=1.5405$ Å was used for calculation. [c]Ref. 12. [d]Ref. 13.

In conclusion, the present Tl(thd) chelate is useful as a potential thallium vapor source for CVD and gas-phase reaction investigations.

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References

1 R. E. Sievers and J. E. Sadlowski, *Science, 201* (1978) 217.
2 Y. Shiokawa, R. Amano, A. Nomura and M. Yagi, *J. Radioanal. Nucl. Chem., 152* (1991) 393.
3 R. Amano and Y. Shiokawa, *J. Radioanal. Nucl. Chem. Lett., 155* (1991) 201.
4 R. Amano, Y. Shiokawa, Y. Suzuki and N. Sato, *J. Radioanal. Nucl. Chem.,* accepted for publication.
5 Y. Shiokawa and R. Amano, unpublished data.
6 R. J. Phollips, M. J. Shane and J. A. Switzer, *J. Mater. Res., 4* (1989) 923.
7 Z. Z. Shang and A. M. Hermann, *Nature (London), 332* (1988) 138.
8 K. J. Eisentraut and R. E. Sievers, *J. Am. Chem. Soc., 87* (1965) 5254.
9 R. Amano, A. Sato and S. Suzuki, *Bull. Chem. Soc. Jpn., 54* (1981) 1368.
10 A. G. Lee, *J. Chem. Soc. A,* (1971) 2007.
11 A. D. Berry, R. T. Holm, R. L. Mowery, N. H. Turner and M. Fatemi, *Chem. Mater., 3* (1991) 72.
12 Joint Committee on Powder Diffraction Standards, *JCPDS File Card No. 6-0486.*
13 *JCPDS File Card No. 8-486.*