THE PROBLEM OF THE STORAGE OF ALKALINE EARTH PRECURSORS CONTAINING 2,2,6,6-TETRAMETHYLHEPTANEDIONE-3,5.

Vyacheslav Vertlib, *[a] **Andrei Drozdov,** [a] **Ivan Timokhin,**[a] **Sergei Troyanov,**[a] **Claudio Pettinari,**[b] **Fabio Marchetti,**[b] **Yo-Sep Min**[c] **and Daesig Kim**[c]

[a] Moscow State University, Chemistry Department, Russia
[b]Dipartimento di Scienze Chimiche, Università degli Studi di Camerino, Italy
[c] Samsung Advanced Institute of Technology, Korea

The important problem of volatility decrease during the storage of barium and strontium 2,2,6,6-tetramethylheptane-dione-3,5 (**Hthd**) derivatives has been studied. Barium complexes were shown more stable to the hydrolysis with respect to analogous strontium derivatives due to the difference in their structure. The cleavage of thd, caused by the partial hydrolysis of the complex has been observed in the case of strontium-containing species. The possible mechanism is proposed. The compound $\{[Ti(thd)_2(\mu^3\text{-}O)(\mu\text{-}Bu^tC(O)CH_2CH_2O)Sr(thd)(\mu\text{-}Bu^tCOO)]_2Sr(Hpz)_2\}$ formed upon the reaction between partially hydrolysed strontium-*thd* derivative and $[Ti(^iPrO)_2(thd)_2]$ has been structurally characterized.

INTRODUCTION

The problem of storage of alkaline earth metal precursors for MOCVD has been poorly studied. Although nearly thirty different strontium and barium chelates have been developed as precursors, the main commercially used species are the derivatives of 2,2,6,6-tetramethylheptanedione-3,5 (**Hthd**) (1). These compounds are oligomers (tetramer in the case of Ba and trimer in the case of strontium) that are very moisture-sensitive due to the coordinative instauration of the metal centre. Their volatility can be improved by formation of adducts $M(\beta\text{-diketonate})_2(L)_n$ (M=Sr, Ba; L = neutral Lewis base as 1,10-phenanthroline, 2,2'-bipyridine and polyethers) having lower nuclearity with respect to that found in binary alkaline earth metal β-diketonates (2, 3). It has been also found that higher coordination numbers increase the stability of the complexes towards hydration and hydrolysis and prolong their guaranteed storage period (4).

The volatility of alkaline earth diketonates decreases upon the prolonged (two or three months) storage. It is likely, that this phenomena is due to the partial degradation of coordinated diketonate ligand, caused by moisture and oxygen, that are allways present in the atmosphere. The full characterization and identification of the degradation products of alkaline earth diketonate precursors is usually complicated because these products are usually non-crystalline. We succeeded in crystallization of one of such products in the form of heterobimetallic complex. For such study we have chosen the mixed ligand complexes with **thd** and a pyrazole, as neutral Lewis base, able to coordinate the central atom in neutral form. Such precursors have the advantage of a low content of carbon, with respect to other Lewis bases already used to protect alkaline-earth metal center from hydration and hydrolysis, which diminishes the carbon contamination of films.

SYNTHESES

The complexes **$[Ba(thd)_2(Hpz)_2]_2$ 1** and **$[Sr(thd)_2(Hpz)_3]$ 2** have been prepared by *in situ* interaction of **Ba** or **Sr** metal respectively with a stoicheometric amount of **Hthd** and the excess of pyrazole in toluene. The solution obtained has been filtered off and concentrated on rotary evaporator.

Analytical data for compound 1

Anal. Calcd. for $C_{28}H_{46}BaN_4O_4$: C, 52.55; H, 7.24; N, 8.75; Ba, 21.46%. Found: C, 52.18; H, 7.40; N, 8.53; Ba, 21.45%.
IR (Nujol, hexachlorobutadiene, cm^{-1}): 3200m, br (NH), 3049 (CH), 2980s, 2910m, 2885m, 1605s, 1590s, 1560s, 1500s (CO, CC), 1480s, 1420s, 1390s, 1220s, 1157m, 1125m, 1042s, 1033s, 949m, 918s, 877s, 862br, 792m, 750s, 728s, 611s, 470 vs, 392s, 377s, 312w. ^{1}H NMR ($CDCl_3$, 300MHz, 295K): δ 1.06 (s, 18 H, $C_4\mathit{H}_{9\mathrm{thd}}$), 5.63 (s, 1 H, $C\mathit{H}_{\mathrm{thd}}$), 6.20 (pt, 1H, H-4_{pz}, ^2J(H-H = 2.1 Hz), 7.41 (pd, 2H, H-3_{pz} + H-5_{pz}), 11.9 (br, 1H, $N\mathit{H}_{\mathrm{pz}}$). ^{1}H NMR ($CDCl_3$, 300MHz, 218K): δ 1.02 (s, 18 H, $C_4\mathit{H}_{9\mathrm{thd}}$), 5.59 (s, 1 H, $C\mathit{H}_{\mathrm{thd}}$), 6.21 (br, 1H, H-4_{pz}), 7.26 (s, 1H, H-3_{pz} or H-5_{pz}), 7.42 (s, 1H, H-3_{pz} or H-5_{pz}), 13.5 (br, 1H, $N\mathit{H}_{\mathrm{pz}}$). ^{13}C NMR ($CDCl_3$, 75 MHz, 295K): δ 28.8 (s, $\mathit{C}H_{3\mathrm{thd}}$), 41.2 ($\mathit{C}(CH_3)_{3\mathrm{thd}}$), 90.0 (s, $\mathit{C}H_{\mathrm{thd}}$), 104.8 ($\mathit{C}4_{\mathrm{pz}}$), 133.2 (s br, $\mathit{C}3_{\mathrm{pz}}$ and $\mathit{C}5_{\mathrm{pz}}$), 199.8 (s, $\mathit{C}O_{\mathrm{thd}}$). ESI MS ($CH_3CN$, 10^{-4} M): (+) 69 (15) [H_2pz^+], 185 (47) [H_2thd^+], 207 (100) [$NaHthd^+$], 223 (55) [$KHthd^+$], 253 (38) [Hthd + Hpz + H^+], 391 (45) [$Na(Hthd)_2^+$]. (-) 183 (100) [thd].

Analytical data for compound 2

Anal. Calcd. for $C_{28}H_{46}N_4O_4Sr$: C, 56.55; H, 7.65; N, 12.76; Sr, 13.31%. Found: C, 56.38; H, 7.40; N, 12.48; Sr, 13.56%. IR (Nujol, hexachlorobutadiene, cm^{-1}): 3200m, br (NH), 2960s, 2923s, 2853m, 2729m, 1595vs, 1576s, 1557m, 1540s, 1505s (CO + CC), 1500sh, 1490s, 1420s, 1359s, 1241s, 1220s, 1184s, 1157m, 1129vs, 1043s, 953m, 924s, 877sh, 864br, 792m, 757s, 730s, 655s, 607vs, 594v, 473vs, 395s, 381s, 359m, 322m. ^{1}H NMR ($CDCl_3$, 300MHz, 295K): δ 1.06 (s, 36H, $C_4\mathit{H}_{9\mathrm{thd}}$), 5.58 (s, 2H, $C\mathit{H}_{\mathrm{thd}}$), 6.23 (pt, 3H, H-4_{pz}, ^2J(H-H = 2.1 Hz), 7.45 (d, 6H, H-

3_{pz} + H-5_{pz}, ^{2}J(H-H = 1.5 Hz), 10.0 (br, 3H, NH_{pz}). ^{1}H NMR (CDCl$_3$, 300MHz, 218K): δ 1.02 (s, 36H, C$_4$$H_{9thd}$), 5.58 (s, 2H, C$H_{thd}$), 6.20 (br, 3H, H-4_{pz}), 7.23 (s, 3H, H-3_{pz} or H-5_{pz}), 7.40 (s, 3H, H-3_{pz} or H-5_{pz}), 13.2 (br, 3H, NH_{pz}). ^{13}C NMR (CDCl$_3$, 75 MHz, 295K): δ 28.6 (s, CH$_{3thd}$), 40.9 (C(CH$_3$)$_{3thd}$), 89.8 (s, CH$_{thd}$), 104.7 ($C4_{pz}$), 133.5 (s br, $C3_{pz}$ and $C5_{pz}$), 199.5 (s, CO$_{thd}$). ESI MS (CH$_3$CN, 10^{-4} M): (+) 185 (47) [H$_2$thd$^+$], 207 (70) [NaHthd$^+$], 223 (100) [KHthd$^+$], 253 (20) [Hthd + Hpz + H$^+$], 391 (45) [Na(Hthd)$_2$$^+$]. (-) 101 (100) [C$_4H_9COO^-$].

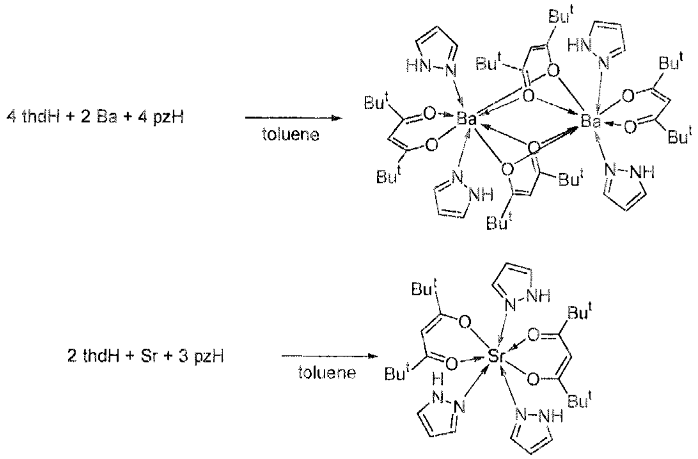
From the reaction between a sample of **2**, stored in closed Wheaton vial for a month and **Ti(Pr^{i}O)$_2$(thd)$_2$** in toluene a colourless crystalline solid **{[Ti(thd)$_2$(μ^3-O)(μ-Bu^{t}C(O)CH$_2$CH$_2$O)Sr(thd)(μ-Bu^{t}COO)]$_2$Sr(Hpz)$_2$}** **3** has been isolated.

Analytical data for compound 3

Anal. Calcd. for C$_{94}$H$_{162}$N$_4$O$_{22}$Sr$_3$Ti$_2$: C, 55.01; H, 7.65; N, 2.89. Found: C, 54.81; H, 7.87; N, 2.72%. IR (Nujol, cm^{-1}): 3600-3570br (NH), 1730m, 1710w, 1690w, 1680-1640w (CO), 1599s 1568s, 1557s, 1537s, 1518vs (CO + CC), 1462s, 1454s, 1422s, 611s, 594m, 473s, 395s, 383s, 325m br (TiO + SrO + SrN). ^{1}H NMR (CDCl$_3$, 300 MHz, 293K): 1.1 (m, 72H, C$_4$$H_{9thd}$ + C$_4$$H_{9piv}$ + C$_4$$H_{9thd}$ + C$_4$$H_{9ketoalcohol}$) 4.43 (s, 2H, C$H_{2ketoalcohol}$), 5.62 (s, 3H, C$H_{thd}$), 6.21 (d, 1H, H-4_{pz}), 7.42 (d, 2H, C-H, H-3_{pz} + H-5_{pz}), 12.2 (br, 1H, NHpz).

RESULTS AND DISCUSSION

The interaction between barium or strontium metals and **Hthd** in the presence of pyrazole (**Hpz**) resulted in the formation of the complexes **1** and **2** (Scheme 1) which are colourless crystalline solids, very soluble in acetone and only slightly less soluble in heptane and hexane.



Scheme 1

They are not so moisture sensitive as **$Ba_4(thd)_8$** (5) and **$Sr_3(thd)_6$** (6) species and can be synthesized on air without using Schlenk techniques.

The structure of **1** consists of dinuclear centrosymmetric molecules **$Ba_2(thd)_4(Hpz)_4$** with eight-coordinated barium atoms (Figure 1). It is likely, that the strontium complex **2** is mononuclear; the strontium atom is being hepta-coordinated.

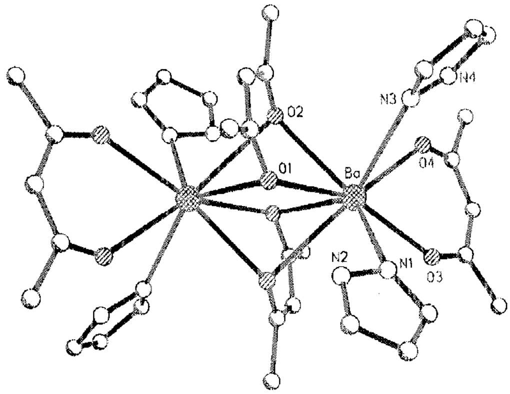


Figure 1

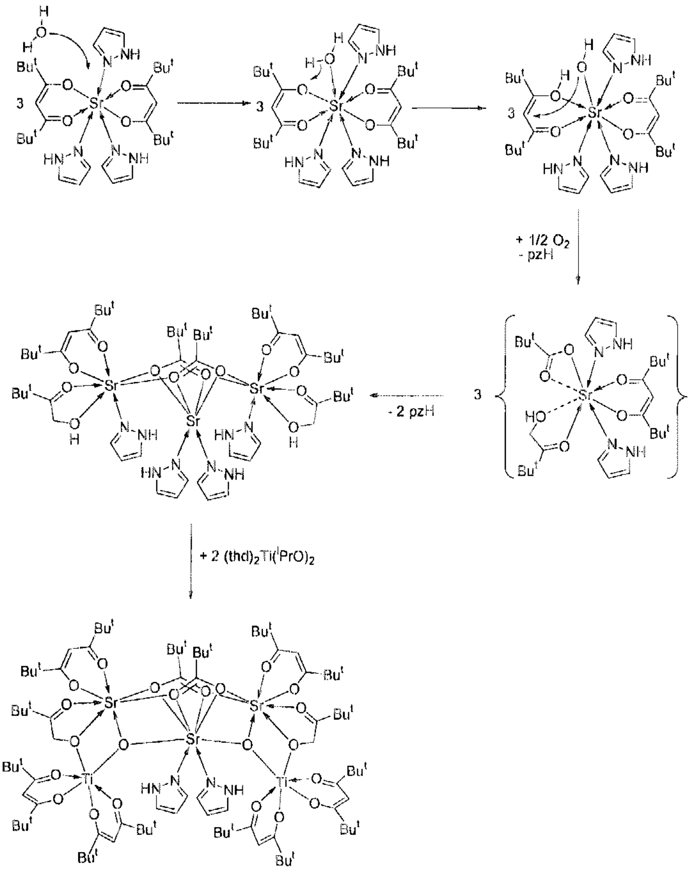
Due to the different structure strontium complex has been shown to be much more sensitive to hydrolysis with respect to barium species. By heating of the compound **2** at 40°C for 3 hours under air, the oil formed slowly turned to yellow. We have studied spectroscopically (IR and ^1H NMR) this oil: there is a major product which signals are coincident with those of the starting compound **2**, together with several side species showing signals of low intensity not only of **thd** and pyrazole, but also of the pivalate $\mathbf{Bu^{t}COO}$ and of the ketoalcoholate $\mathbf{Bu^{t}COCH_2O}$, arising from decomposition of some **thd**, likely coordinated to strontium. By prolonged heating on air, the intensity of signals due to the formation of these by-products increases and that of **2** decreases, indicating that the latter is slightly thermally unstable to the decomposition and that some coordinated **thd** undergo $C(O)\text{-}C_{\alpha}$ breaking in the presence of oxygen with formation of the corresponding pivalate $\mathbf{Bu^{t}COO}$ and 1-hydroxy-3,3-dimethylbutan-2-one $\mathbf{Bu^{t}COCH_2OH}$. These species are the products of hydrolysis followed by Claisen retro-condensation. Such proceses have been earlier studied for fluorinated diketones to form trifluoroacetates (7 - 9) The high-yielded synthesis of trifluoroacetates starting from hexafluoroacetylacetone has also been reported (10). In the previous studies the formation of mixed ligand pivalate-*thd* complexes has been ascribed to the presence of the impurity of pivalic acid in the 2,2,6,6-tetramethylheptane-dione-3,5 (11), but in our case it is obvious that it is produced by the breaking of the ligand.

In fact prolonged heating of **2** carried out in absence of air and in rigorous anhydrous conditions doesn't afford any decomposition product. Attempts to separate and to characterize these by-products failed, likely due to their very similar solubility in many solvents.

By prolonged exposition to air at room temperature, the powder of **2** becomes oil with the slight odour of **Hthd**. The presence of free diketone is confirmed by NMR spectra of the product. A part of **Hthd** likely remains coordinated to strontium and, in the presence of oxygen from air and due to basic media, affords the oxidation cleavage with the formation of pivalate and ketoalcohol that coordinate the metal center. The formation of neutral diketone ligands coordinated to metal in the basic media is well known for complexes of transition metals (12).

Taking into consideration the trimeric structures of strontium complexes with **thd** we can assume that one of the main products of the former oily mixture is a trimer (Scheme 2). Nevertheless we failed to crystallize it from the reaction mixture.

Studying the possibility to create a heterometallic Sr-Ti species suitable for single-course CVD of BSTO thin films we performed the interaction of **1** and **2** with $\mathbf{Ti(^{i}PrO)_2(thd)_2}$. From the reaction of **1** with $\mathbf{Ti({}_{i}PrO)_2(thd)_2}$, the starting material **1** and $\mathbf{[Ti(\mu\text{-}O)(thd)_2]}$ resulted from the hydrolysis of the **Ti** precursor being the species recovered after prolonged reaction. Freshly prepared **2** also doesn't react with $\mathbf{Ti(^{i}PrO)_2(thd)_2}$, but using a sample stored in Wheaton vial for a month we isolated a small amount of colourless needles characterized as the heterometallic derivative $\mathbf{\{[Ti(thd)_2(\mu^3\text{-}O)(\mu\text{-}Bu^{t}C(O)CH_2CH_2O)Sr(thd)(\mu\text{-}Bu^{t}COO)]_2Sr(Hpz)_2\}}$ **(compound 3)**.



Scheme 2

The single crystal X-ray measurements showed the compound 3 was formed by symmetric Sr_3Ti_2 units (Figure 2).

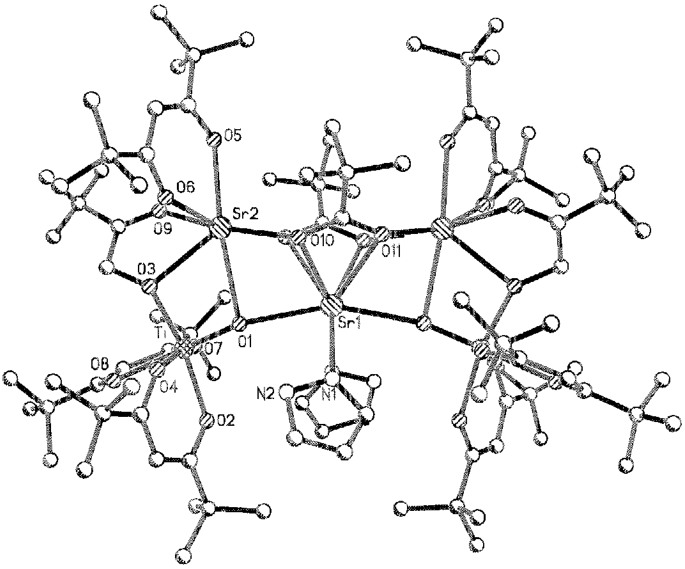


Figure 2

VOLATILITY

The thermogravimetry studies of **1** and **2** in vacuo have been performed. Both complexes (Figure 3) are volatile. On sublimation at 10^{-3} torr they undergo the dissociation to pyrazole and strontium or barium tetramethylheptanedionate.

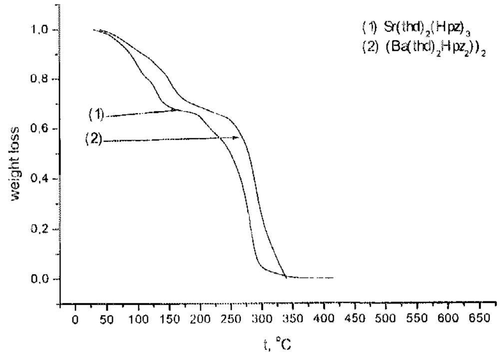


Figure 3

CONCLUSIONS

The reaction of strontium and barium with **Hthd** and pyrazole gives mononuclear strontium and dinuclear barium derivatives with the azole acting as neutral ancillary ligand. The presence of pyrazole stabilizes barium toward hydrolysis with respect to **$Ba_4(thd)_8$** The strontium complex **2** are shown to be sufficiently sensitive to hydrolysis. On the basis of spectroscopic and structural data it was shown that hydrolysis causes the cleavage of *thd*-ligand and the formation of pivalate-containing oligomeric species. It was shown that **$Ti(^iPrO)_2(thd)_2$** doesn't react with alkaline-earth metal diketonates in the absence of base, but reacts with hydrolized strontium species to give heterometallic compound.

Acknowledgments

Thanks are due to the university of Camerino, "Carima Foundation", INTAS (individual grant YS-220 for Dr Andrei Drozdov and research project 00-469) and Russian Fund of Basic Research (research grant 00-03-32662) for financial support. This work was also supported by grant from Samsung Advanced Institute of Technology.

References

(1) D.J. Otway, W.S. Rees Jr, *Coord. Chem. Rev.*, **210**, 279 (2000)
(2) S.R. Drake, M.B. Hursthouse, K.M.A. Malik, S.A.S. Miller, *J. Chem. Soc., Chem. Comm*, 478 (1993)
(3) N. Kuzmina, M. Ryazanov, S. Troyanov, *Polyhedron*, **18**, 2177 (1999)
(4) A. Drozdov, S. Troyanov, *Main.Group Met.Chem.*,**19**, 547 (1996)
(5) J.J. Brooks, H.O.Davies, T.J. Leedham, A.C Jones, A. Steiner, *Chem. Vap. Deposition.*, **6**, 66 (2000)
(6) A Gleizes, S. Sans-Lenain, D.Medus, *Compt. Rend. Sci. Paris, Ser. II*, **313**, 761 (1991)
(7) S.J. Pradilla, H.W Chen, F.W. Koknat, J.P.Jr Fackler, *Inorg. Chem.*, **18**, 3519 (1979)
(8) S.R Drake, A. Lyons, D.J Otway, D.J. Williams, *Inorg. Chem.*, **33**, 1230 (1994)
(9) O. Poncelet, L.G. Hubert-Pfalzgraf, J.C. Daran, *Polyhedron*, **9**, 1305 (1990)
(10) M. Urrutigoïty, C. Cecutti, F. Senocq, J.-P. Gorrichon, A. Gleizes, *Inorg. Chim. Acta*, **248**, 15 (1996)
(11) A. Drozdov, S. Troyanov, A. Pisarevsky, Yu. Struchkov *Polyhedron*, **13**, 1445 (1994)
(12) T. Agapie, P.L. Diaconescu, D.J. Mindiola, C.C. Cummins, *Organometallics*, **21**, 1329 (2002)