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From mono- to poly-nuclear heteroleptic alkaline earth-titanium complexes containing 2,2,6,6-tetramethylheptane-3,5-dionate (thd) and pyrazole (Hpz) or 3,5-dimethylpyrazole (Hpz*) ligands. Synthesis, spectroscopic and structural characterization of $[Ba(thd)_2(Hpz)_2]_2$, $[Sr(thd)_2(Hpz^*)_3]$, $[Ba(thd)_2(Hpz^*)_2]_2$ and the heterometallic $\{[Ti(thd)_2(\mu^3\text{-}O)(\mu\text{-}Bu^tC(O)CH_2CH_2O)Sr(thd)(\mu\text{-}Bu^tCOO)]_2Sr(Hpz)_2\}$

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Abstract

By interaction of Ba or Sr metals with 2,2,6,6-tetramethylheptane-3,5-dione (Hthd) and pyrazole (Hpz) or 3,5-dimethylpyrazole (Hpz*), the volatile compounds $[M(thd)_2(L)_n]_m$ (**1**–**4**) (**1**: $m=2$, $n=2$, L = Hpz, M = Ba; **2**: $m=1$, $n=3$, L = Hpz, M = Sr; **3**: $m=2$, $n=2$, L = Hpz*, M = Ba; **4**: $m=1$, $n=3$, L = Hpz*, M = Sr) have been obtained. They have been characterized by analytical and spectral methods (IR, ^1H and ^{13}C NMR, ESI MS spectroscopy). They are shown to be fluxional at room temperature in $CDCl_3$ solution. The crystal structures of **1** and **3** consist of centrosymmetric dinuclear species with two 8-coordinate Ba centers, each surrounded by a chelating terminal thd, two bridging thd and two monodentate L. Whereas the structure of the strontium derivative **4** is mononuclear; hepta-coordination of Sr being due to two chelating thd and three monodentate Hpz*. $[Sr(thd)_2(Hpz)_3]$ (**2**) interacts with $[Ti(^iPrO)_2(thd)_2]$ yielding the heterometallic compound $\{[Ti(thd)_2(\mu^3\text{-}O)(\mu\text{-}Bu^tC(O)CH_2CH_2O)Sr(thd)(\mu\text{-}Bu^t\text{-}COO)]_2Sr(Hpz)_2\}$ (**5**) upon cleavage of the diketonate ligand thd (retro-Claisen condensation). In **5**, the strontium atoms are linked with each other by tetradentate pivalate groups with μ^2-oxygen atoms and by oxo-bridges also bonded to $Ti(thd)_2$ moiety together with chelating bridging ketoalkoxide groups. When the reaction between $[Ba(thd)_2(Hpz)_2]$ (**1**) and $[Ti(^iPrO)_2(thd)_2]$ was carried out, the dinuclear $[Ti(\mu\text{-}O)(thd)_2]_2\cdot 0.5Hpz$ (**6**) was the only species identified.

Keywords: 2,2,6,6-Tetramethylheptane-3,5-dionate; Pyrazole; 3,5-Dimethylpyrazole; MOCVD; Sr; Ba; ESI spectroscopy

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1. Introduction

The discovery of interesting electric and magnetic properties in several mixed metal oxides has prompted great interest in the synthesis and characterization of suitable molecular precursors for the preparation of new ceramics by MOCVD or sol–gel processes [1–4]. It is well established that, for obtaining mixed metal oxides

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by these methods, the use of a “single source” precursor containing different metals in the desired stoichiometry constitutes a synthetic strategy in order to increase the quality of the final material [5]. Therefore, the starting problem is the synthesis of heterometallic compounds with the required ratios of the metals. Alkoxo- and diketonato-ligands have been recognized as anionic ligands of choice due to their tendency to enhance, respectively, solubility and volatility [6–8]. The volatility can be improved by the formation of adducts such as M(β-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 [6,9,10]. It has also been found that higher coordination numbers increase the stability of the complexes towards hydration and hydrolysis and prolong their guaranteed storage period [6,11].

The mixed Group 2 metal titanates are useful sol–gel precursors in the preparation of dense ferroelectric materials, thin-film electronic components and piezoelectric devices [12]. In this contest, barium—β-diketonates are known to react with titanium alkoxides affording heteroleptic barium–titanium complexes [13]; however, the interaction between barium or strontium β-diketonate adducts and titanium-alkoxide β-diketonates has not been studied yet. The study of such interactions can disclose new horizons, as barium and strontium—β-diketonate adducts and titanium-alkoxide—β-diketonates are employed as precursors in the fabrication of thin films of barium strontium titanium oxide (BSTO), Ba$_x$Sr$_{1-x}$TiO$_3$, one of the most promising dielectric materials for a capacitor in giga-bit dynamic random access memories (DRAMs) by MOCVD [14]. Moreover, also heteroleptic barium–titanium and strontium–titanium complexes are reported as BSTO thin films MOCVD precursors [13] and as sol–gel precursors for BSTO piezoelectric phase fabrication [15].

On the basis of these findings, we have decided to start a systematic investigation on the synthesis of new heterometallic Ti–Ba and Ti–Sr precursors for MOCVD and sol–gel techniques containing alkoxides and β-diketonate as anionic ligands and a series of differently substituted azoles, as neutral Lewis bases, able to coordinate the central atom in neutral form taking 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.

Here we report the synthesis, structural and spectroscopic characterization of four volatile adducts [Ba(thd)$_2$(L)$_2$]$_2$ and [Sr(thd)$_2$(L)$_3$] (Hthd = 2,2,6,6-tetramethylheptane-3,5-dione, L = pyrazole, Hpz or 3,5-dimethylpyrazole, Hpz*) and their interaction with Ti(^{i}PrO)$_2$(thd)$_2$ [16], a model substance to study the formation of heterobimetallic species due to its wide employment for deposition of titanium-containing thin films. The formation of the first known strontium–titanium heterobimetallic complex containing thd, Hpz, oxo, pivalate and ketoalcoholate ligands, the latter two derived from unexpected breaking of thd ligands, is described.

2. Experimental

2.1. Materials and methods

Solvents were used as supplied or distilled using standard methods. The samples for microanalyses were dried in vacuum to constant weight (293 K, ca. 0.1 Torr). Elemental analyses (C, H, N) were performed inhouse with Fisons Instruments 1108 CHNS-O Elemental Analyser. The barium and strontium contents were determined by gravimetry in form of BaSO$_4$ and SrSO$_4$. IR spectra were recorded from 4000 to 100 cm^{-1} using a Perkin–Elmer System 2000 FT-IR instrument. ^{1}H NMR spectra were recorded on a VXR-400 Varian spectrometer operating at 400 MHz or on VXR-300 Varian operating at 300 MHz. Proton and carbon chemical shifts are reported in ppm vs Me$_4$Si. Melting points were taken on an SMP3 Stuart scientific instrument and on a capillary apparatus. Thermogravimetric analysis was performed on an OD-102 derivatograph under nitrogen atmosphere with a heating rate of 5 °C min^{-1} and on ‘Sinku–Riko’ thermal analyzer under vacuum (0.01 Torr) with a heating rate of 10 °C min^{-1}. Pyrazole (Hpz), 3,5-dimethylpyrazole (Hpz*), barium and strontium were purchased from Aldrich (Milwaukee) and 2,2,6,6-tetramethylheptane-3,5-dione (Hthd) from Fluka and used as received. The quality of Hthd was carefully controlled by ^{1}H NMR spectroscopy, and no signals of impurities were detected. 3,5-Di-*tert*-butylpyrazole was synthesized from Hthd by a standard method [17]. Ti(^{i}PrO)$_2$(thd)$_2$ was obtained from Ti(^{i}PrO)$_4$ (Aldrich) as described in Ref. [16] and purified by vacuum sublimation. The positive and negative electrospray mass spectra were obtained with a Series 1100 MSI detector HP spectrometer, using an acetonitrile mobile phase. Solutions for electrospray ionization mass spectrometry (ESI-MS) were prepared using reagent grade acetone or acetonitrile. For the ESI-MS data, mass and intensities were compared to those calculated using IsoPro Isotopic Abundance Simulator, version 2.1 [18].

2.2. Syntheses

2.2.1. $[Ba(thd)_2(Hpz)_2]_2$ (**1**)

2,2,6,6-Tetramethylheptane-3,5-dione (Hthd) (1.33 g, 7.23 mmol) and barium metal (0.494 g, 3.6 mmol) were added to a toluene solution (30 ml) of pyrazole (Hpz) (0.49 g, 7.23 mmol). The resulted mixture was stirred under a slight heating during approximately 5 h, until barium dissolved completely. The solution obtained was filtered off and concentrated on the rotary evaporator. Large crystals of **1** (2.1 g, 86.7% yield) were formed from the resulted solution in a week, which were then separated and dried in vacuo. m.p. 100–103 °C. Anal. Calcd. for $C_{28}H_{46}BaN_4O_4$: C, 52.55; H, 7.24; Ba, 21.46; N, 8.75. Found: C, 52.18; H, 7.40; Ba, 21.45; N, 8.53%. 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, 470vs, 392s, 377s, 312w. ^{1}H NMR ($CDCl_3$, 300 MHz, 295 K): δ 1.06 (s, 18H, C_4H_{9thd}), 5.63 (s, 1H, CH_{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, NH_{pz}). ^{1}H NMR ($CDCl_3$, 300 MHz, 218 K): δ 1.02 (s, 18H, C_4H_{9thd}), 5.59 (s, 1H, CH_{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, NH_{pz}). ^{13}C NMR ($CDCl_3$, 75 MHz, 295 K): δ 28.8 (s, CH_{3thd}), 41.2 ($C(CH_3)_{3thd}$), 90.0 (s, CH_{thd}), 104.8 ($C4_{pz}$), 133.2 (s br, $C3_{pz}$ and $C5_{pz}$), 199.8 (s, CO_{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].

2.2.2. $[Sr(thd)_2(Hpz)_3]$ (**2**)

Compound **2** (89% yield) was obtained by using the same procedure described for **1**. Compound **2** forms supersaturated solutions and it has been recrystallized by cooling the toluene solution up to −196 °C (liquid nitrogen); m.p. 88–90 °C. Anal. Calcd. for $C_{31}H_{50}N_6O_4Sr$: 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 ($CDCl_3$, 300 MHz, 295 K): δ 1.06 (s, 36H, C_4H_{9thd}), 5.58 (s, 2H, CH_{thd}), 6.23 (pt, 3H, H-4_{pz}, $^2J_{H-H} = 2.1$ Hz), 7.45 (d, 6H, H-$3_{pz}+H$-5_{pz}, $^2J_{H-H} = 1.5$ Hz), 10.0 (br, 3H, NH_{pz}). ^{1}H NMR ($CDCl_3$, 300 MHz, 218 K): δ 1.02 (s, 36H, C_4H_{9thd}), 5.58 (s, 2H, CH_{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, 295 K): 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_3CN, 10^{-4} M): (+) 185 (47) [H_2thd^+], 207 (70) [$NaHthd^+$], 223 (100) [$KHthd^+$], 253 (20) [$Hthd+Hpz+H^+$], 391 (45) [$Na(Hthd)_2^+$]; (−) 101 (100) [$C_4H_9COO^-$].

2.2.3. $[Ba(thd)_2(Hpz^*)_2]_2$ (**3**)

Compound **3** (76% yield) was prepared as described for **1**; m.p. 153–155 °C. Anal. Calcd. for $C_{32}H_{54}BaN_4O_4$: C, 55.21; H, 7.82; N, 8.05; Sr, 19.73. Found: C, 55.25; H, 8.03; N, 7.81; Sr, 19.6%. IR (Nujol, hexachlorobutadiene, cm^{-1}): 3300br (NH), 3188br (CH), 1590s, 1574m, 1567m, 1557m, 1548sh, 1538m, 1531m, 1520m, 1515m, 1504m (CO, CC), 1460br, 1455s, 1376m, 1338sh, 1286m, 1214m, 1177m, 1122m, 1005m, 949w, 930w, 860m, 787m, 731m, 660m, 620m, 592m, 476s, 407m, 391m, 371w. ^{1}H NMR ($CDCl_3$, 300 MHz, 295 K): δ 1.06 (s, 36 H, C_4H_{9thd}), 2.18 (s, 12H, CH_{3pz}), 5.61 (s, 2H, CH_{thd}), 5.75 (s, 2H, H-4_{pz}), 10.8 (br, 2H, NH_{pz}). ^{1}H NMR ($CDCl_3$, 300 MHz, 218 K): δ 1.02 (s, 18H, C_4H_{9thd}), 5.58 (s, 1H, CH_{thd}), 6.20 (br, 1H, H-4_{pz}), 7.23 (s, 1H, H-3_{pz} or H-5_{pz}), 7.40 (s, 1H, H-3_{pz} or H-5_{pz}), 13.2 (br, 1H, NH_{pz}). ^{13}C NMR ($CDCl_3$, 75 MHz, 295 K): δ 12.0 (s br, CH_{3pz}), 28.7 (s, CH_{3thd}), 41.0 (s, $C(CH_3)_{3thd}$), 89.5 (s, CH_{thd}), 104.1 ($C4_{pz}$), 199.3 (s, CO_{thd}). ESI-MS (CH_3CN, 10^{-4} M): (+) 97 (100) (H_2pz^+), 185 (5) [H_2thd^+], 207 (55) [$NaHthd^+$], 223 (28) [$KHthd^+$], 281 (10) [$Hthd+Hpz^*+H^+$], 391 (18) [$Na(Hthd)_2^+$]; (−) 95 (100) [pz^{*-}].

2.2.4. $[Sr(thd)_2(Hpz^*)_3]$ (**4**)

Compound **4** (72% yield) was prepared as described for **2**; m.p. 69–71 °C. Anal. Calcd. for $C_{37}H_{62}N_6O_4Sr$: C, 59.85; H, 8.42; N, 11.32; Sr, 11.80. Found: C, 59.33; H, 8.73; N, 11.09; Sr, 11.7%. IR (Nujol, hexachlorobutadiene, cm^{-1}): 3200br, 3180br (NH), 3160m (CH), 1592s, 1580m, 1566sh, 1538m, 1515m (CO, CC), 1330m, 1289m, 1230w, 1221w, 1140m, 1006m, 949w, 950w, 862m, 787m, 730sh, 719mm, 662m, 620sh, 592m, 470s, 408m, 391m, 371sh, 350m, 305w, 279w. ^{1}H NMR ($CDCl_3$, 300 MHz, 295 K): δ 1.11 (s, 36H, C_4H_{9thd}), 2.14 (s, 18H, CH_{3pz}), 5.58 (s, 2H, CH_{thd}), 5.72 (s, 3H, H-4_{pz}), 11.2 (br, 2H, NH_{pz}). ^{1}H NMR ($CDCl_3$, 300 MHz, 218 K): δ 1.02 (s, 18H, C_4H_{9thd}), 5.58 (s, 1H, CH_{thd}), 6.20 (br, 1H, H-4_{pz}), 7.23 (s, 1H, H-3_{pz} or H-5_{pz}), 7.40 (s, 1H, H-3_{pz} or H-5_{pz}), 13.2 (br, 1H, NH_{pz}). ^{13}C NMR ($CDCl_3$, 75 MHz, 295 K): δ 12.1 (s br, CH_{3pz}), 28.7 (s, CH_{3thd}), 41.0 (s, $C(CH_3)_{3thd}$), 89.5 (s, CH_{thd}), 104.1 ($C4_{pz}$), 199.3 (s, CO_{thd}). ESI-MS (CH_3CN, 10^{-4} M): (+) 97 (100) (H_2pz^+), 207 (20) [$NaHthd^+$], 223 (20) [$KHthd^+$], 281 (10) [$Hthd+Hpz^*+H^+$], 391 (18) [$Na(Hthd)_2^+$]; (−) 101 (100) [$C_4H_9COO^-$].

2.2.5. $\{[Ti(thd)_2(\mu^3\text{-}O)(\mu\text{-}Bu^tC(O)CH_2CH_2O)Sr(thd)(\mu\text{-}Bu^tCOO)]_2Sr(Hpz)_2\}$ (**5**)

$Ti(^iPrO)_2(thd)_2$ (4.5 g, 8.47 mmol) was added to 5.0 g (8.47 mmol) of **2** dissolved in 30 ml of toluene. The solution was stirred for 5 h and then evaporated to dryness to give a yellow oil which crystallizes slowly at room temperature to form the colorless needles. It was crystallized rapidly by immediate cooling up to − 196 °C (liquid nitrogen). Crystals of **5** in 10% yield suitable for X-ray structural studies were obtained by slowly cooling the supersaturated solution from 60 to 20 °C during 16 h. Anal. Calcd. for $C_{94}H_{162}N_4O_{22}Sr_3Ti_2$: 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, 293 K): 1.1 (m, 72H, $C_4H_{9\mathrm{thd}}+C_4H_{9\mathrm{piv}}+C_4H_{9\mathrm{thd}}+C_4H_{9\mathrm{ketoalcohol}}$, 4.43 (s, 2H, $CH_{2\mathrm{ketoalcohol}}$), 5.62 (s, 3H, CH_{thd}), 6.21 (d, 1H, H-4_{pz}), 7.42 (d, 2H, C–H, H-$3_{\mathrm{pz}}+H$-5_{pz}), 12.2 (br, 1H, NHpz).

2.2.6. $[Ti(\mu\text{-}O)(thd)_2]_2\cdot 0.5Hpz$ (**6**)

To 6.39 g (10 mmol) of **1** dissolved in 30 ml of toluene, 5.32 g (10 mmol) of $Ti(^iPrO)_2(thd)_2$ was added under violent stirring. The resulting solution formed was stirred for 3 h and then evaporated to dryness giving a pale yellow oil that was crystallized by cooling it up to − 196 °C (liquid nitrogen). Recrystallization of the crude product from toluene afforded **6** as colorless crystals in 20% yield. Anal. Calcd. for $C_{45.5}H_{78}NO_2Ti_2$: C, 71.26; H, 10.25; N, 1.83. Found: C, 71.55; H, 10.65; N, 1.72%. IR (Nujol, cm^{-1}): 1599s, 1568s, 1557s, 1518vs (CO, CC), 1462s, 1454s, 1422s, 611s, 594m, 473s, 395s, 383s, 325m br (TiO). ^{1}H NMR ($CDCl_3$, 300 MHz, 293 K): 1.1 (m, 72H), 5.62 (s, 4H, CH_{thd}), 6.21 (d, 1H, H-4_{pz}), 7.42 (d, 2H, C–H, H-$3_{\mathrm{pz}}+H$-5_{pz}), 12.2 (br, 1H, NHpz). The tetrameric $[Ti(\mu\text{-}O)(thd)_2]_4$ has been previously reported and characterized [19].

2.2.7. Single-crystal X-ray structure determination

Data collection for crystals of **1**, **3**, **4**, **5** and **6** was carried out at low temperature on an IPDS (Stoe) diffractometer using graphite monochromated Mo Kα radiation ($\lambda = 0.71973$ Å). Numerical absorption correction based on the crystal shape was applied for **4** only. Structure solutions and refinements were carried out by using SHELXS-97 [20] and SHELXL-97 [21] programs. Details of data collection and refinement are given in Table 1. Non-hydrogen atoms were refined anisotropically by full-matrix least-squares techniques based on F^2. Some Bu^t-groups in structure **3** were disordered over two positions with approximately equal occupancies. Hydrogen atoms were placed at the calculated positions and were included in the final refinements in a riding mode. Selected bond lengths and angles for **1**, **3**, **4** and **5** are listed in Tables 2–4.

Table 1
Crystallographic data and details of structure refinements for compounds **1**, **3**, **4** and **5**

Compound	**1**	**3**	**4**	**5**
Formula	$C_{56}H_{92}Ba_2N_8O_8$	$C_{32}H_{54}BaN_4O_4$	$C_{37}H_{59}N_6O_4Sr$	$C_{94}H_{160}N_4O_{22}Sr_3Ti_2$
Molecular weight	1280.06	696.13	739.52	2056.92
Crystal system	triclinic	monoclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$C2/c$
a (Å)	11.356(2)	14.104(3)	10.948(2)	12.146(3)
b (Å)	13.474(3)	13.118(3)	12.367(3)	26.886(5)
c (Å)	13.566(3)	19.832(4)	17.357(4)	35.134(7)
α (deg)	118.81(3)	90.00	77.85(3)	90.00
β (deg)	108.09(3)	95.33(3)	74.17(3)	95.13(3)
γ (deg)	97.08(3)	90.00	68.45(3)	90.00
V (Å^3)	1633.5(6)	3653.4(14)	2086.8(8)	11427(4)
Z	1	4	2	4
d_{calc} (g cm^{-3})	1.301	1.266	1.177	1.196
μ (mm^{-1})	1.250	1.123	1.3330	1.585
Crystal dimensions (mm^3)	0.50 × 0.30 × 0.15	0.60 × 0.50 × 0.20	0.35 × 0.20 × 0.10	0.50 × 0.20 × 0.05
T (K)	180(2)	180(2)	180(2)	180(2)
$\theta_{\max}$ (deg)	26.0	26.7	26.0	25.4
Reflections collected	14 004	27 627	10 087	32 083
Reflections unique	6478	7387	7031	10 410
Reflections with $I > 2\sigma(I)$	4994	6393	5086	4188
Data/parameters	5333/346	7387/452	7031/451	10 410/589
wR_2 (F^2)	0.0667	0.0611	0.1086	0.1202
R_1	0.0205	0.0231	0.0452	0.0559
Largest peak and hole in ΔF (e Å^{-3})	0.88/ − 0.88	0.73/ − 0.61	0.54/ − 0.70	0.65/ − 0.83

Table 2
Selected bond lengths (Å) and angles (°) for compounds **1** and **3**

Compound	**1**	**3**
Bond distances		
Ba–O1	2.8301(15), 2.981(2)	2.7220(15), 2.8769(15)
Ba–O2	2.718(2), 2.882(2)	2.8443(14), 3.0244(15)
Ba–O3	2.617(2)	2.6151(16)
Ba–O4	2.712(2)	2.7041(15)
Ba–N1	2.897(2)	2.9071(17)
Ba–N3	2.932(2)	2.8771(15)
Bond angles		
O1–Ba–O1	93.58(4)	89.51(4)
O1–Ba–O2	64.84(4), 58.90(5), 58.85(5), 60.97(5)	65.73(4), 58.57(4), 61.55(4), 59.13(4)
O1–Ba–O3	101.30(5), 146.37(4)	147.37(4), 107.54(5)
O1–Ba–O4	97.04(5), 143.63(4)	85.04(4), 146.91(4)
O2–Ba–O2	89.45(4)	94.73(3)
O2–Ba–O3	101.69(5), 154.47(5)	98.89(4), 154.06(4)
O2–Ba–O4	94.94(5), 150.70(4)	89.15(4)137.14(4)
O3–Ba–O4	64.36(5)	65.36(5)
O1–Ba–N1	68.61(6), 130.08(5)	86.86(5), 142.14(5)
O1–Ba–N3	79.85(6), 138.13(5)	72.83(5), 126.56(5)
O2–Ba–N1	126.67(6), 72.06(6)	147.31(5), 84.84(5)
O2–Ba–N3	76.85(5), 139.76(5)	68.86(5), 130.92(5)
O3–Ba–N1	78.82(6)	95.15(6)
O3–Ba–N3	106.76(6)	85.61(5)
O4–Ba–N1	125.35(6)	70.20(5)
O4–Ba–N3	69.11(6)	134.76(5)
N3–Ba–N1	86.08(6)	79.33(6)
Ba–O1–Ba	86.42(4)	90.49(4)
Ba–O2–Ba	90.55(4)	85.27(3)

Table 3
Selected bond lengths (Å) and angles (°) for compound **4**

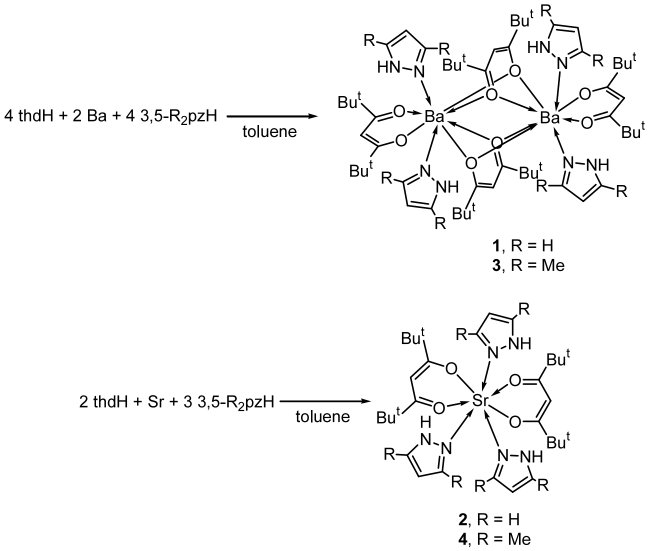
Bond distances	
Sr–O1	2.560(3)
Sr–O2	2.452(2)
Sr–O3	2.483(2)
Sr–O4	2.600(2)
Sr–N1	2.650(3)
Sr–N3	2.670(3)
Sr–N5	2.750(3)
Bond distances	
O1–Sr–O2	69.23(8)
O1–Sr–O3	127.95(8)
O1–Sr–O4	158.15(8)
O2–Sr–O3	81.61(8)
O2–Sr–O4	132.28(8)
O3–Sr–O4	67.21(7)
O1–Sr–N1	103.59(9)
O1–Sr–N3	75.15(9)
O1–Sr–N5	86.63(9)
O2–Sr–N1	87.08
O2–Sr–N3	119.73(9)
O2–Sr–N5	145.35(9)
O3–Sr–N1	117.31(9)
O3–Sr–N3	84.15(9)
O3–Sr–N5	132.88(9)
O4–Sr–N1	77.18(9)
O4–Sr–N3	92.90(9)
O4–Sr–N5	72.42(9)
N1–Sr–N3	148.98(9)
N1–Sr–N5	74.48(10)
N3–Sr–N5	74.50(9)

Table 4
Selected bond lengths (Å) and angles (°) for compound **5**

Bond distances			
Sr1–O1	2.560(3)	Sr1–N1	2.644(6)
Sr1–O8	2.663(4)	Sr1–O9	2.686(4)
Sr2–O2	2.430(3)	Sr2–O3	2.425(4)
Sr2–O8	2.508(4)	Sr2–O9	2.510(4)
Sr2–O10	2.527(4)	Sr2–O11	2.649(6)
Sr2–O1	2.662(3)	Ti–O1	1.707(4)
Ti–O4	2.190(4)	Ti–O5	2.010(4)
Ti–O6	2.060(3)	Ti–O7	2.002(4)
Ti–O10	1.923(3)		
Bond angles			
O1–Sr1–O1	158.66(14)	O1–Sr1–N1	87.38(15)
O1–Sr1–N1	77.39(15)	N1–Sr1–N1	89.1(3)
O1–Sr1–O8	73.81(11)	O1–Sr1–O8	122.21(12)
N1–Sr1–O8	92.09(16)	N1–Sr1–O8	160.40(15)
O8–Sr1–O8	93.33(17)	O1–Sr1–O9	122.93(11)
O8–Sr1–O9	70.79(13)	O8–Sr1–O9	49.22(11)
O8–Sr2–O10	130.23(12)	O3–Sr2–O1	116.31(12)
O9–Sr–O10	112.05(12)	O2–Sr2–O1	171.72(14)
O1–Ti–O6	96.80(16)	O1–Ti–O4	177.33(19)
O1–Ti–O5	96.36(18)	O1–Ti–O7	99.94(19)
O6–Ti–O4	82.58(14)	O10–Ti–O4	87.05(15)

3. Results and discussion

The interaction between barium or strontium metals and Hthd in the presence of pyrazole (Hpz) or 3,5-dimethylpyrazole (Hpz*) resulted in the formation of the complexes **1**–**4** (Scheme 1) which are colourless crystalline solids, very soluble in acetone and only slightly less soluble in heptane and hexane. They are sufficiently stable to moisture with respect to $Ba_4(thd)_8$ [22] and $Sr_3(thd)_6$ [7] species and can be synthesized on air without using Schlenk techniques. In the IR spectra of **1**–**4**, the ν(C–O, C–C) bands at 1500–1600 cm^{-1} clearly indicate the bidentate-chelating mode of the thd as already found in analogous barium and strontium β-diketonates derivatives containing N-donor Lewis bases [23–26]. In the ^{1}H NMR spectra of **1**–**4**, the thd, Hpz and Hpz* resonances are shifted downfield with respect to the free ligand that confirms the coordination. Moreover, there is always one set of signals due to the thd and pyrazole moieties, respectively, according to fluxionality around the metal. On cooling the samples **1** and **2** at 218 K, the doublet at approximately 7.40 ppm, due to both H_3 and H_5 of the pirazole, splits into two doublet and the broad signal of the N–H shifts to lower fields, indicating the well-known metallotropic–prototropic exchange is not operating at low temperature [27].



Scheme 1.

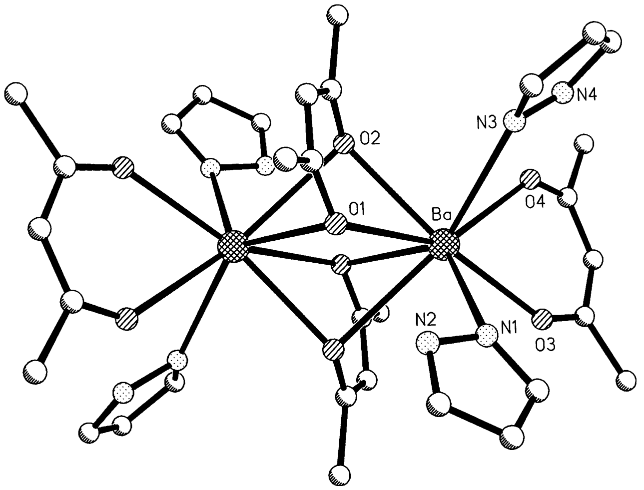


Fig. 1. Molecular structure of derivative **1**.

On the other hand, at 218 K both the methyl and methyne protons give a sharp singlet slightly shifted to higher field as compared with free Hthd, suggesting that fluxionality of thd around the metal center occurs also at low temperature, differently from that previously observed for [$Mg_2(thd)_4$] [28]. When complexes **1**–**4** were exposed to air, the ^{1}H spectra change so that two peaks originating from the methyl and the methyne protons appear due to the free Hthd.

The influence of the substituents in **3** and **5** positions of pyrazole on the formation of metal complexes was further investigated. The 3,5-di-*tert*-butylpyrazole is not able to coordinate metal centers at all, mainly due to the steric hindrance of the bulky *tert*-butyl groups, binary Ba and Sr diketonates being generally recovered from the reaction mixture.

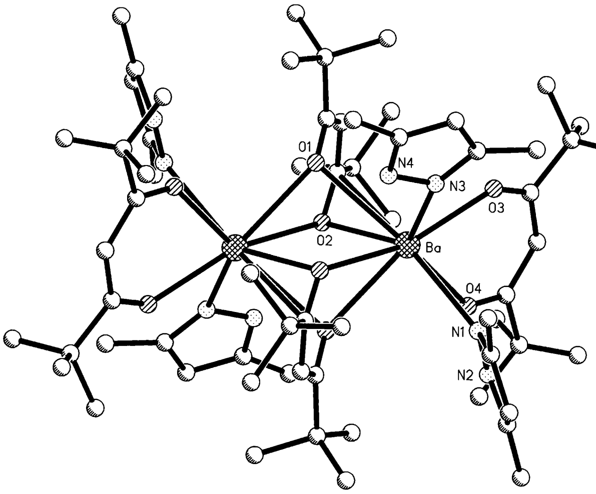


Fig. 2. Molecular structure of derivative **3**.

While barium derivatives **1** and **3** easily crystallize from the reaction mixture and do not need further purification, the reactions between strontium, Hthd and pyrazoles usually form oils, which can be crystallized only by cooling the flask in liquid nitrogen. The pure compounds **2** and **4** are obtained by recrystallization of the solidified oil from toluene.

The structures of **1**, **3** and **4** were determined by X-ray single-crystal crystallography. The most important bond distances are listed in Tables 2 and 3. The structures of **1** and **3** (Figs. 1 and 2) consist of dinuclear centrosymmetric molecules $Ba_2(thd)_4(L)_4$ (L = Hpz or Hpz*). Barium atoms are 8-coordinate by three thd groups and two pyrazole molecules. Among the four thd groups in the molecule, two are bidentate chelating and other two are tetradentate bridging. The same coordination pattern has been earlier reported in the adducts with NH_3 [24], Et_2O [29] and dipy [23] and in the adducts of barium acylpyrazolonate with water and imidazole [30]. The Ba–O(1),O(2) distances (2.718(2)–2.981(2) Å, avg. 2.853(2) Å in **1** and 2.722(2)–3.024(2) Å, avg. 2.86(2) Å in **3**) are in the range typical for Ba-thd complexes with the same coordination pattern. Other crystallographically independent thd ligands in both structures are bidentate chelating with average Ba–O distances of 2.665(2) Å in **1** and 2.660(1) Å in **3**. The pyrazole molecules in the structures are neutral monodenate ligands with average Ba–N distances of 2.91(2) Å in **1** and 2.88(1) Å in **3** that can be compared with Ba-N(imidazole) distance in dimer in acylpyrazolones (2.790(3) Å) [30]. The presence of methyl substituents in pyrazole in **3** causes only slight elongation of Ba–O and Ba–N distances with respect to **1**.

On the contrary to the previously described barium unit the strontium complex **4** is mononuclear (Fig. 3). The strontium atom is hepta-coordinate, which is not typical for diketonate derivatives with neutral ancillary

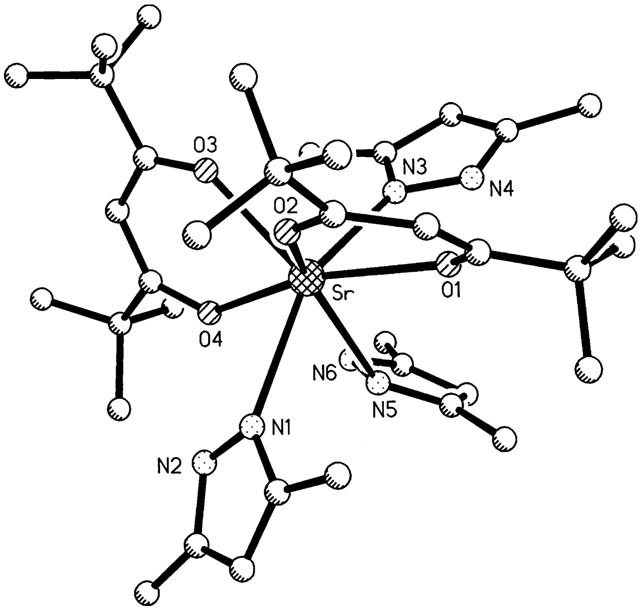


Fig. 3. Molecular structure of derivative **4**.

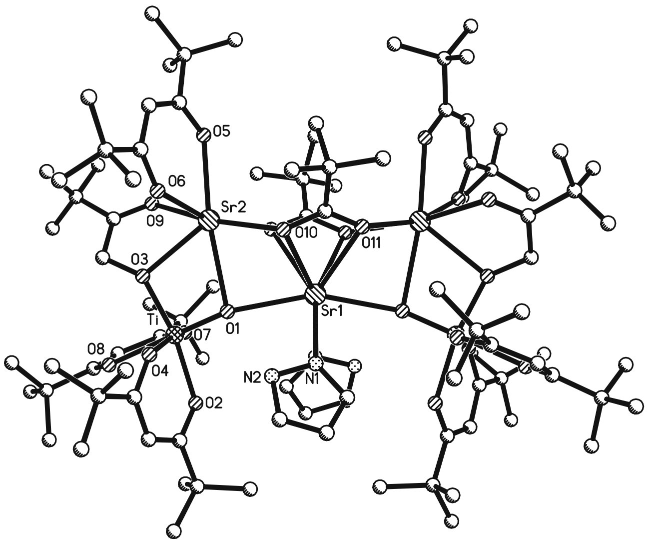


Fig. 4. Molecular structure of derivative **5**.

ligands. Its coordination environment is formed by four oxygens from two chelating thd-anions and three molecules of Hpz. The Sr–O(thd) distances are in the range 2.452(2)–2.600(2) Å (average 2.524(2) Å) that are typical for mononuclear strontium complexes [9,25,31–33]. The three pyrazole ligands coordinate the metal center in monodentate mode with Sr–N distances of 2.650(3)–2.750(3) Å (avg. 2.690(3) Å) that are apparently shorter than those found in the similar derivatives with polyamines (> 2.70 Å) due to the difference in coordination numbers of strontium [34].

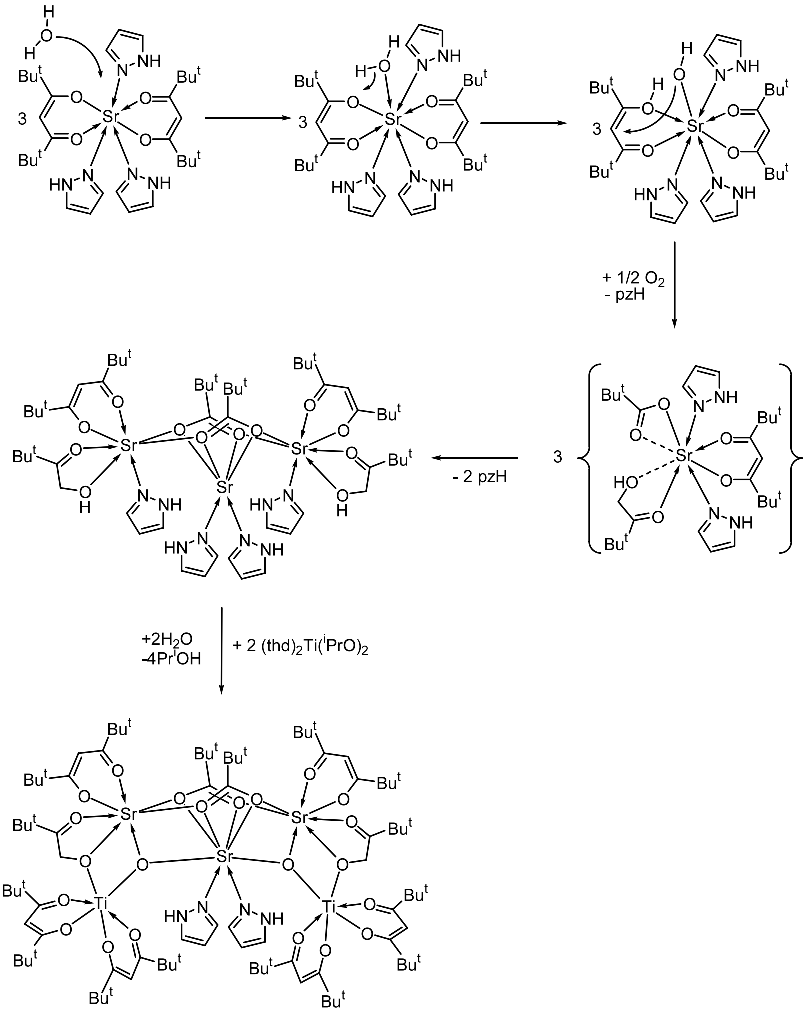
From the reaction of **2** with preformed $Ti(Pr^iO)_2(thd)_2$ in toluene, a colorless derivative, characterized as the heterometallic derivative **5**, was obtained, after cooling the reaction mixture. Derivative **5** is a colourless crystalline solid very soluble in all commonly used aprotic solvents. The presence of the ν(C–O) bands at 1700–1680 cm^{-1} in the IR spectrum of **5** indicates the mode of carboxyl and carbonyl groups of *tert*-butylcarboxylate (piv) and the anion of 1-hydroxy-3,3-dimethylbutan-2-one, resulted from splitting of thd ligand. The ^1H NMR spectrum confirms the existence of both *tert*-butylcarboxylate (piv) and the anion of 1-hydroxy-3,3-dimethylbutan-2-one groups.

The X-ray crystal structure of **5** has been determined. **5** contains symmetric Sr_3Ti_2 units (Fig. 4). The strontium atoms are linked with each other by tetradentate μ^2-pivalates groups and oxo-bridges while they are linked to titanium by the same oxo-bridges and chelating bridging ketoalkoxide. It is well known that diketonate ions have lower tendency to act as bridging with respect to alkoxides or carboxylates [6,35]. The ability of pivalate to held the alkaline earth metals in oligonuclear units or infinite chains is also well known and has been earlier reported by us [22b,23,36]. Two strontium atoms of the trimer are crystallographically equal (Sr2) and heptacoordinate, each being coordinated by a bidentate chelating thd-ligand, a deprotonated tridentate chelating α-ketoalcohol, two O-atoms from bridging pivalates and by oxo-group (μ-O). The Sr–O(thd) distances (Table 4) are typical for heptacoordinate strontium in complexes with thd [37]. Another crystallographically independent strontium atom (Sr(1)) shows a coordination number (CN) 8 and is chelated by two pivalate anions, two oxo-groups and two monodentate pyrazole molecules. Both titanium atoms in the complex are equivalent. The coordination sphere of each Ti can be described as a distorted octahedron formed by oxygen atoms of two chelating thd-ligands, an oxo-atom and an alkoxy-group of ketoalkoxide.

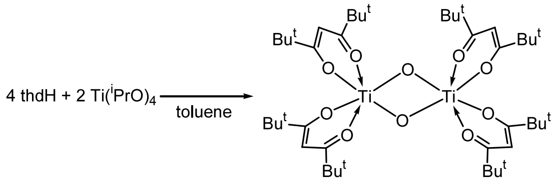
The deprotonated pivalic acid and 3,3-dimethyl-1-hydroxobutanone-2 present in the structure in the stoichiometry 1:1 are clearly products of retro-Claisen condensation that occurred by heating the reaction mixture. In the literature are known some examples of cleavage of diketonate ligands during the complex formation, however this was not a subject of special study. The most known example is the cleavage of the fluorinated diketones to form trifluoroacetates [38]. The high-yielded synthesis of trifluoroacetates starting from hexafluoroacetylacetone has also been reported [39]. In the previous studies, the formation of mixed ligand pivalate-thd complexes has been ascribed to the presence of impurity of pivalic acid in the dipivaloylmethane employed [36] but in our case it is obvious that it is produced by the breaking of the ligand.

In order to give further insight into this decomposition process and into the formation of compound **5**, we have performed some additional experiments. Firstly, by heating of compound **2** at 40 °C for 3 h, the oil formed slowly turned to yellow. We have studied spectroscopically (IR and ^{1}H 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 carboxylate Bu^{t}COO and of the ketoalkoxide Bu^{t}COCH$_2$OH, arising from decomposition of some thd, likely coordinated to strontium. By prolonged heating on air, the intensity of signals due to these by-products increases and that of **2** decreases, indicating that the latter are slightly termically unstable to decomposition and that some coordinated thd undergo C(O)–C$_\alpha$ breaking in the presence of oxygen with formation of the corresponding pivalate Bu^{t}COO and 1-hydroxy-3,3-dimethylbutan-2-one Bu^{t}CO-CH$_2$OH. These species are the products of hydrolysis followed by Claisen retro-condensation. In fact prolonged heating of **2** carried out in the absence of air and in rigorous anhydrous conditions does not afford any decomposition product. Attempts to separate and characterize these by-products failed, likely due to their very similar solubility in many solvents.

Additionally, 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 spectrum 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 [40]. The retro-Claisen condensation of such type can be catalyzed by bases or enzymes [41] or metal complexes [42]. The presence of titanium could accelerate this process, as Ti complexes have been recently shown to cause the radical scission of symmetrical 1,4-dicarbonyls. The reactive



Scheme 2.



Scheme 3.

species that cause the cleavage were shown to be titanium-bound amido-enolates [43].

Taking into consideration the trimeric structures of strontium complexes with thd and the presence of the trimeric Sr fragments in the structure of **5**, we can assume one of the main products of the former oily mixture to be a trimer (Scheme 2). The presence of $Ti(Pr^iO)_2(thd)_2$ in the reaction mixture accelerates the process. The oxo-bridges present in the structure resulted from hydrolysis that caused the complete evolution of Pr^iOH. It is worth to note that in inert atmosphere and without heating that prevent hydrolysis of initial strontium species, the formation of derivative **5** does not occur.

From the reaction of **1** with $Ti(Pr^iO)_2(thd)_2$, no analogous Ba–Ti heterometallic species have been obtained; the starting material **1** and $[Ti(\mu\text{-}O)(thd)_2]_2\cdot 0.5Hpz$ (**6**) resulted from the hydrolysis of the Ti precursor being the species recovered after prolonged reaction (Scheme 3). The X-ray crystal structure of **6** was preliminary investigated (with $R_1 = 0.12$) which surprisingly shows the compound to be dimeric with two μ_2-O bridging groups, different from the tetrameric species earlier reported with thd and acylpyrazolonate [44], but similar to that reported with acac (acacH = acetylacetone) [45].

Preliminary thermogravimetric studies were performed on derivatives **1**, **2** and **5**. The temperature dependence of mass loss in vacuo for **1** and **2** is shown in Fig. 5, whereas thermogravimetric data for **1** and **2** are reported in Table 5. The two process found can be ascribed to loss of the pyrazole ligands and sublimation of the M-thd species, respectively. The sublimation of the Sr–Ti species **5** was also investigated at the temperature range 20–250 °C in vacuo (Fig. 6). Three different zones can be identified that can be assigned to loss of the pyrazole (**1**), evolution of the $[TiO(thd)_2]_n$ compounds (**2**), followed by sublimation of alkaline earth metal tetramethylheptanedionate-pivalate species (**3**).

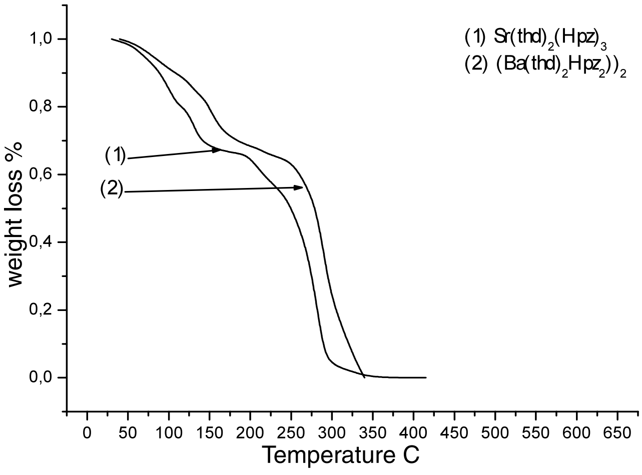


Fig. 5. The temperature dependence of mass loss in vacuo for (1) Sr compound and (2) Ba compound.

Table 5
Thermogravimetric data for compounds **1** and **2**

Compound	ΔT (°C)	Δm (%)	Nature of the effect
1	0–255	22.04	loss of the Hpz
1	255–490	77.96	sublimation of the $Ba(thd)_2$
2	0–255	31.03	loss of the Hpz
2	255–530	68.97	sublimation of the $Sr(thd)_2$

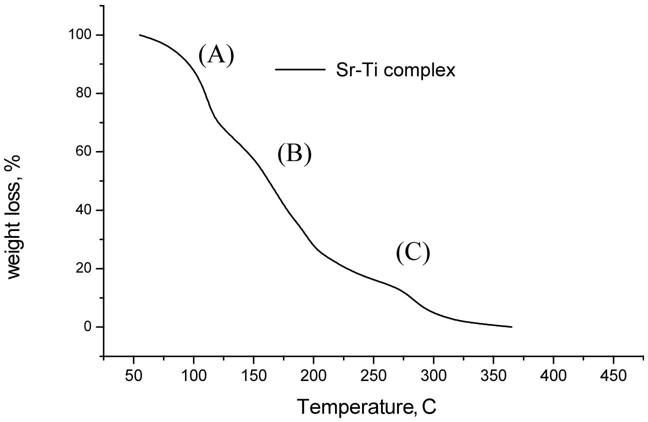


Fig. 6. The temperature dependence of mass loss in vacuo for derivative **5**.

4. Conclusions

The reaction of strontium and barium with Hthd and pyrazoles gives mononuclear strontium and dinuclear barium derivatives with the azole acting as neutral ancillary ligand. The presence of pyrazole highly stabilizes barium toward hydrolysis while the analogous strontium complexes remain air-sensitive to moisture. On the basis of spectroscopic and structural data, it was shown that hydrolysis causes the cleavage of thd ligand to pivalate and ketoalkohol, followed by the formation of pivalate-bridging oligomeric species. We can suppose that the strontium diketonates with other ancillary ligands, but not only pyrazoles, decompose on air by the analogous mechanism. It was found that

$Ti(OiPr)_2(thd)_2$ does not react with alkaline earth metal diketonates in the absence of base, but reacts with hydrolyzed strontium species to give heterometallic compound.

5. Supplementary material

Details of data collection, refinement, atom coordinates, anisotropic displacement parameters, and bond lengths and angles for complexes **1**, **3**, **4** and **5**. This material has been deposited with the Crystallographic Data Center as Supplementary Publication Nos 200491 (**1**), 200493 (**3**), 200492 (**4**) and 200494 (**5**). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: +44-1223-336-033 or e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgements

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