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Group 2 element β-diketonate complexes: synthetic and structural investigations

David J. Otway, William S. Rees Jr *

School of Chemistry and Biochemistry,
School of Materials Science and Engineering and the Molecular Design Institute,
Georgia Institute of Technology, Atlanta, GA 0332-0400, USA

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Abbreviations: Dec, decomposes; Des, desolvates; Di, diglyme, $CH_3O(CH_2CH_2O)_2CH_3$; β-Diket, β-diketonate; diki-, $Bu^tCOCHCN\{(CH_2CH_2O)_2Me\}Me$; Dme, dimethoxyethane, monoglyme, $CH_3OCH_2CH_2OCH_3$; Dmf, dimethylformamide; Dptriki-, $Bu^tCOCHCN\{(CH_2CH_2O)_3Me\}Bu^t$; DSC, differential scanning calorimetry; EI^+, electron impact, positive mode (mass spectrometry condition); Et_2O, diethylether; EtOH, ethanol, C_2H_5OH; FAB^+, fast atom bombardment, positive mode (mass spectrometry condition); Hacac, 2,4-pentanedione, acetylacetone; $HOAr_N$, HOC_6H_3-2,6-$(CH_2NMe_2)_2$; Hbdmap, bisdimethylaminopropanol; Hdfhd, 1,1,1,2,2,6,6,7,7,7-decafluoro-3,5-heptanedione; Hdmppd, 2,2-dimethyl-4-phenyl-3,5-pentanedione; Hdnppd, 1,3-di(dinitro)phenyl-1,3-propanedione; Hdppd, 1,3-diphenyl-1,3-propanedione; Hept, heptaglyme, $CH_3O(CH_2CH_2O)_7CH_3$; Hfod, 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione; Hhfac, 1,1,1,5,5,5-hexafluoro-2,4-pentanedione, hexafluoroacetlyacetonate; Hmteta, $Me_2NCH_2CH_2N\{Me\}CH_2CH_2N\{Me\}CH_2CH_2NMe_2$, hexamethyl-triethylenediamine; Hofhd, 1,1,1,2,2,6,6,6-octafluoro 3,5-hexandione; Hpta, pivaloyltrifluoroacetylacetonate or 1,1,1-trifluoro-5,5-dimethyl-2,4-hexanedione; Hpfdmhd, 1,1,1,2,2-pentafluoro-6,6,-dimethyl-3,5-heptanedione; Htclac, 1,1,1-trichloro-2,4-pentanedione; Htdfnd, 1,1,1,2,2,3,3,7,7,8,8,9,9,9-tetradecafluoro-4,6-nonanedione; Htfac, 1,1,1-trifluoro-2,4-pentanedione, trifluoroacetlyacetonate; Htmhd, 2,2,6,6-tetramethyl-3,5-heptanedione, dipivaloylmethane; $m/e+$, mass/charge ratio, (mass spectrometry condition); MOCVD, metallorganic chemical vapor deposition; m.p., melting point; NEt_3, triethylamine; ns, not soluble; Ph, phenyl group; Piv, pivalic acid; Pmdeta, $Me_2NCH_2CH_2N\{Me\}CH_2CH_2NMe_2$, pentamethyldiethylenetriamine; Py, pyridine; S, soluble; Sls, slightly soluble; STA, simultaneous thermal analysis; Tet, tetraglyme, $CH_3O(CH_2CH_2O)_4CH_3$; TGA, thermogravimetric analysis; Thf, tetrahydrofuran; Tmeda, tetramethlyethylenediamine; Tri, triglyme, $CH_3O(CH_2CH_2O)_3CH_3$; YBCO, yttrium barium copper oxid.

* Corresponding author. Tel.: + 1-404-8944049; fax: + 1-404-8941144.

E-mail addresses: will.rees@chemistry.gatech.edu (W.S. Rees Jr); d.j.otway@ic.ac.uk (D.J. Otway)

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Abstract

An overview of the Group 2 element β-diketonates is presented, including their synthesis, structural characteristics, physical properties, and some potential applications. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Group 2 element; β Diketonate; Synthetic and structural investigations; MOCVD

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1. Introduction

Metal β-diketonates M(RCOCHCOR)$_x$ (where R, alkyl; aryl etc., and the R groups are not necessarily equivalent) are amongst the most widely studied coordination compounds and their chemistry has been investigated for most of the metals in the periodic table [1]. The coordination tendencies of the ligand (i.e. to form chelates with the metal and delocalize the negative charge over a 'metallocycle') are well established and a large number of publications have appeared [2,3]. Variations of the R groups often influence the properties of this class of compounds. Apart from the bonding and structural aspects associated with these complexes, the ability of these ligands to 'wrap-up' a variety of metals has provided inorganic chemists with examples of compounds of electropositive metal ions which portray covalent characteristics, i.e. solubilities in organic solvents and high volatilities. These special characteristics have been extensively exploited in the past for solvent extraction and gas–liquid chromatographic techniques [4,5]. Interest in metal β-diketonate complexes also arises from their application as contact shift reagents for the enhanced resolution of non-magnetic resonance (NMR) spectra, in laser technology and in the polymer industry [1]. The presence of trace quantities of β-diketonate complexes in fuels [6–8] has also aroused interest. Several reviews have been published in this area, [9–13] as well an excellent book by Bradley, Mehrotra and Gaur [1].

More recently, the quest for the production of high quality oxide thin films by metal organic chemical vapor deposition (MOCVD) has led workers to explore β-diketonate complexes as potential molecular precursors [149]. In general, such precursors must be volatile, have sufficient stability to transport to the deposition site, and decompose cleanly to give the desired material. An additional advantage of the metal β-diketonate complexes is that they often exhibit greater hydrolytic stability than their respective alkoxide counterparts. A range of β-diketonate complexes of both main group and transition metals have been used to deposit films of metals, [14] metal oxides, [14] metal sulfides, [15] and metal fluorides [14]. However, the deposition of Group 2 element containing oxides, and sulfides, has been hampered by the relatively poor volatilities and thermal stabilities of the Group 2 element β-diketonate precursors. Consequently, this has led to a renaissance within the area, partially due to their potential utility as MOCVD precursors for Group 2 element containing electronic materials such as $YBa_2Cu_3O_{7-x}$, [16–24] SrS:Ce, [25] $Ba_{1-x}Sr_xTiO_3$, [26–28] and this area has experienced rapid development in the last 3 years. Thus, the scope of this review article is that of the Group 2 element β-diketonates, their synthesis, structural characteristics, physical properties, and some potential. As of now, there have been no reports of radium complexes with β-diketones synthesized.

2. Syntheses of β-diketone ligands

β-Diketones are capable of keto–enol tautomerism, the tautomers exist in equilibrium with each other in solution (Fig. 1), and structurally they possess a *cis* configuration and *syn* conformation. Under appropriate conditions the enolic hydrogen atom of the β-diketone may be replaced by a metal cation to produce a six-membered metallocycle, thereby shifting the keto–enol equilibrium in favor of the enol form. The position of the keto-enol equilibrium for each differs according to the electronic characteristics of the substituents. Some of the more commonly utilized syntheses to β-diketone ligands are described below.

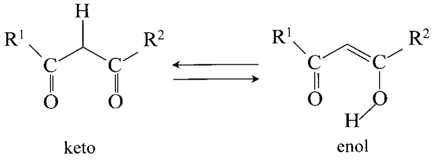


Fig. 1. Keto–enol tautomerism in β-diketones.

2.1. Formation of β-diketones via sulfur extrusion

Thioesters containing a β-keto group in the alkyl position can be converted to β-diketones by treatment of the ligand with a tertiary phosphine under basic conditions [29]. The starting thioesters themselves may be prepared by the reaction between a thiol acid and an α-haloketone [30].

2.2. β-Diketones from α,β-epoxyketones

β-Diketone ligands can be prepared by heating α,β-epoxyketones at 80–140°C in toluene with small amounts of a tetrakis(triphenylphosphine)palladium catalyst and DPPE [31]. This reaction is a rearrangement of a single ring to a single site of unsaturation.

2.3. β-Diketones from α-diazo-β-hydroxyketones

α-Diazo-β-hydroxyketones, obtained by the condensation of aldehydes with 1-diazo-1-lithioacetone, can be transformed into the corresponding β-diketone ligands with a rhodium(II) acetate catalyst [32].

2.4. β-Diketones from acyl cyanides and lithium enolates

β-Diketones may be prepared by the reaction of acyl cyanides with ketone enolates, which are formed using lithium diisopropylamide as a base [33].

2.5. β-Diketones via boroxazines

Enol boranes readily undergo cycloaddition with nitriles under mild conditions to produce boroxazines, which may then undergo hydrolysis to the corresponding β-diketone ligands [34]. This reaction is applicable to a wide variety of R groups, and readily allows for the synthesis of either centrally substituted or unsubstituted β-diketones.

2.6. β-Diketones utilizing organocopper catalysts

Selective C-acylation can usually be achieved by quenching organocuprate-generated enolates with acid chlorides using ether as a solvent [35]. C-, O-diacylated products are often obtained as well, but these rapidly undergo hydrolysis to give the β-diketone.

2.7. β-Diketones from the acylation of ketones with anhydrides

Ketones may be acylated by anhydrides with a BF_3 catalyst, to give a β-diketone. With unsymmetrical diketones, acylation usually occurs on the more highly substituted side. The actual product is a complex containing BF_2^-, which can be decomposed by aqueous sodium acetate to give the β-diketone.

2.8. β-Diketones from the acylation of ketones by acid chlorides

A ketone having an α-hydrogen may be acylated with an acid chloride in pyridine to form a β-diketone.

2.9. β-Diketones from the acylation of ketones by esters (Claissen condensation)

A predominant route to β-diketones is the acylation of ketones by esters. The relatively low reactivity of the ester carbonyl group generally means that alkali-metal hydroxides or hydrides must be utilized as condensing reagents. Although many ketones may be acylated with esters, there are some limitations to the reaction. Ketones which possess an α-methylene group can usually be acylated at that position with oxalic or formic esters, and sometimes with ethyl acetate, phenyl or methyl benzoate, and certain other esters [36,37]. In the case of acetone, which has an α-methyl group on both sides, there is a tendency towards acylation of both methyl positions to yield an α,β,γ-triketone.

2.10. β-Diketones from the amines

Recently (1995), there was a report on the synthesis of a range of β-diketones by Sokolov et al. [38]. They react acetylinic ketones with amines, then follow this by hydrolysis of the resulting aminovinylketones to give some 1,3-diketones. The yields are relatively high, and for those diketones that are difficult to synthesize via a Claissen condensation, this may be considered an alternative route.

All of the above methods may be utilized to prepare a variety of β-diketones; however, the Claissen condensation reaction is generally the method of choice because of its overall efficiency. It requires only one step and provides for reasonably high yields (60–80%). The starting materials are also readily obtainable. In comparison to the other methods available, which require multiple steps, more expensive starting materials and lower overall yields, Claissen condensation reactions are, in general, able to yield the desired compounds in a cost-effective (both time and money) manner. Virtually all the β-diketone ligands described herein may be purchased from a commercial vendors (e.g. Lancaster Synthesis, Aldrich), whilst the exceptions to this rule are synthesized via Claissen condensation reactions.

3. General syntheses of metal β-diketonates

3.1. Direct routes

The direct syntheses of metal β-diketonates may be achieved from a number of sources (M, MO_x, MCl_x, $M(CO_3)_x$, MH_x; see Mehrotra et al. [1] for an overview of these syntheses). Similar constraints may be placed on the source used as for the synthesis of metal alkoxides.

3.2. From metal alkoxides

Metal alkoxides will undergo exchange reactions with β-diketones in a stoichiometric fashion. The advantage of this synthetic route over direct methods is that the isolation of very pure materials is rendered possible if enough care is taken in the preparation of the starting metal alkoxide materials (i.e. the use of anhydrous, oxygen free solvents and rigorous handling techniques), e.g. [39,40].

$$[\mathrm{Ti(OPr}^i)_4] + n(\beta\text{-diket}) \overset{\text{hexane}}{\rightarrow} [(\mathrm{Pr}^i\mathrm{O})_{4-n}\mathrm{Ti}(\beta\text{-diket})_n]_x + n\mathrm{Pr}^i\mathrm{OH}$$

Thus, it is possible to synthesize a range of materials via this route with their properties tailored as required.

3.3. Metathesis

For example.

$$TiCl_4 + 4KL \rightarrow 4KCl + TiL_4$$

4. General reactivity of metal β-diketonates

There are a number of chemical reactions that may occur with metal β-diketonates and again these have been reviewed by Mehrotra et al. [1]. Examples of some of these reactions are summarized below.

4.1. Electrophilic substitution reactions

A wide variety of ligands will react with the 3-carbon atom of a six-membered chelate ring, substituting the proton with an electrophile, for example Fig. 2 (where X^+, Cl; Br; NO_2; NCS; $COCH_3$; COOH etc.).

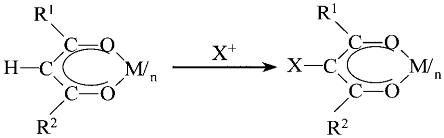


Fig. 2. Electrophilic substitution reactions of metal β-diketonates.

A complete discussion of these reactions may be found in [1] together with conditions and work up details.

4.2. Adduct formation

Many different types of Lewis base ligands will coordinate to a metal β-diketonate complex and these reactions have shown to help to break down the degree of oligomerization of some of the higher coordinate metals e.g. Groups 1, 2 and the lanthanides [41].

Reactions of this type are known for most metal chelates with a wide range of materials reported to date for most of the metals in the periodic table. This strategy has proved to be very useful in the further 'tailoring' of such chelate systems with respect to their usage as molecular precursors. This strategy only works when the charge on the metal is such that $2 \times (\text{charge}) < \text{optimum coordination number}$. When it is not, then the latent Lewis acidity of the metal supplies the energy for adduct formation. Both entropy and enthalpy play a large role herein.

5. Coordination modes observed in metal β-diketonates

As with the metal alkoxides, a wide range of coordination modes has been observed for β-diketonate ligands in metal complexes. The degree of bridging is determined by the metal, the steric bulk of the ligand itself and whether or not any Lewis bases are present. Thus for instance, $[Mn(acac)_3]$ [42] is a monomer in the solid state with purely chelating β-diketonate ligands whereas $[Pr(tmhd)_3]_2$ (even though the bulky β-diketonate tetramethyl-3,5-heptanedionate, tmhd, is used) is a dimeric solid with chelating and bridging tmhd ligands [43].

In complexes with large atomic radii metals, like caesium, strontium or barium, a number of bonding modes of the β-diketonate ligands may be observed. Most researchers in this field have reached agreement that the predominate interatomic interactions in these complexes are electrostatic (i.e. ionic) in nature, with current data lending little support for covalency in metal ligand bonding. Nevertheless, it is indispensable in examining the complexes discussed herein to be capable of depicting interatomic connectivity's. Thus, as with the broad area of boron hydrides, one does not associate each 'line of connectivity' with a localized two-electron bond. The Lewis acidity and consequent electron deficiency of most metal centers in their β-diketonate complexes enables the metals to form oligomers through the bridging properties of the β-diketonate ligand. The ability of these ligands to bridge metal centers arises from the fact that L^- utilizes only one each lone pair electron per oxygen atom in primary bonding, and therefore has one each lone pair electron per oxygen atom available for employment in the secondary interaction. The degree of oligomerization is dependent on a number of factors, including.

1. The size of the metal. The larger the ionic radii of the metal, the higher the density of coordination sites around it, and thus bridging β-diketonate linkages are favored over terminal ones.

2. The more electron deficient metals encourage greater oligomerization. Therefore, electropositive metals often form large aggregates.
3. The steric effects of the β-diketonate ligand are important.

The heavier Group 2 metals have low charge density ratios, and they have a pronounced tendency to expand their coordination sphere. This can give rise to aggregates via the bridging of coordinated β-diketonate ligands. The average coordination numbers observed for strontium and barium complexes are 6–8, but both metals have been observed to form complexes with a coordination number as low as 3 (for M–N only bonded systems, not M–O) and as high as 9 (for Sr) and 12 (for Ba).

β-Diketonates, with their ability to chelate to the metal center, prove to be very adept at also bridging (via the lone pairs on the oxygen atoms) to other metal centers to help to fill their coordination spheres. A comprehensive study of some of these complexes has revealed six main coordination modes for such ligands and they are illustrated in Fig. 3. The bonding modes 4, 5 and 6 are more rare than the first three, and are only usually observed in large aggregates of metals with a large coordination sphere, e.g. $[Ba_4(tmhd)_8]$ [44–47].

As noted above this aggregation may be broken down by the addition of a Lewis base.

As mentioned above, an extensive overview of the literature published in 1978 has been undertaken by Mehrotra et al. [1] in his book and the reader is referred to this publication for further details of early Group 2 element β-diketonate complexes.

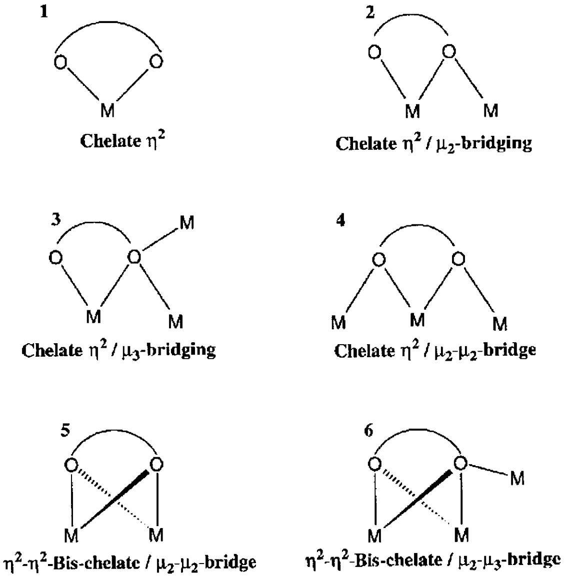


Fig. 3. Bonding modes of metal β-diketonates.

6. Group 2 element β-diketonate complexes

In general, the heavier Group 2 element β-diketonate compounds are oligomeric or polymeric, which may account for their decreased volatilities. They readily form addition compounds with Lewis bases resulting in a decrease in the degree of oligomerization/polymerization. This point is particularly significant, since the corresponding Group 2 element alkoxide derivatives prefer to expand their coordination number through alkoxy bridging interactions rather than by addition of a Lewis base; [48] this may be due to the chelate effect of the β-diketonate ligand. Furthermore, if sterically encumbered ligands, such as tmhd or hexafluoro-2,4-pentanedionate (hfac), are used in association with Lewis bases then discrete molecular crystalline solids may be obtained.

The basic groundwork in the area was laid out by Hammond in the 1960's, [49] with the syntheses of the compounds 'M(tmhd)$_2$' and 'M(dppd)$_2$'. These compounds are placed in quotation marks since they were isolated from ethanolic solutions. They are probably ethanol solvates or may be even more complex {see, for example, the recent complex [Ba$_5$(O)(tmhd)$_5$(Htmhd)$_4$(OH)$_3$] (Fig. 4) synthesized from Ba(OH)$_2$ in water} [50,51]. Mass spectrometric studies of the simple [M(acac)$_2$]$_n$ compounds were carried out by MacDonald et al. [52] in the late 1960's and the gas chromatographic properties of the [M(tmhd)$_2$]$_n$ compounds were also studied at this time [53]. A number of these compounds have been structurally characterized and will be discussed later.

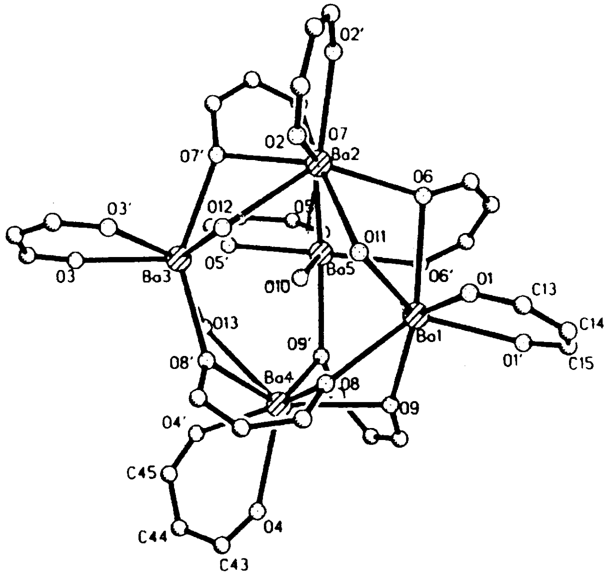


Fig. 4. Molecular structure of [Ba$_5$(O)(tmhd)$_5$(Htmhd)$_4$(OH)$_3$] [50,51]. The central barium is six coordinate and the other barium centers are seven coordinate. The molecule's overall geometry may be best described as a distorted square based pyramid.

With the discovery of superconducting metal oxides by Bednorz and Müller in 1986, [54] the area of metal oxide precursor research was revitalized. In the period from 1988 onwards, a steadily increasing amount of work was published on chelates of the Group 2 elements, especially those involving barium [55]. The situation in late 1991 was summed up thus.

'Although many alkaline-earth metal β-diketonate chelates were synthesized a decade or two ago, these compounds need further characterization with respect to their structures, volatilities and thermal stabilities, particularly in the light of their great importance to the MOCVD of superconducting films' [50,51].

Thus in the following few years, a greatly increasing number of publications have seen print in this rapidly expanding area, as it is one of great current interest to chemists and materials scientists alike.

7. General discussion

The synthesis of Group 2 element chelates has created numerous problems for researchers in this area of chemistry for a number of years. A typical problem (mentioned above) is the contamination of the products by water (or other Lewis bases), as the unadducted complexes are very prone to the uptake of coordinating solvents. The reason for this is the large atomic radii of the metal 2+ ions, and their associated Lewis acidity. Thus, for example the synthesis of '$Ba(tmhd)_2$' from $Ba(OH)_2$ and Htmhd in water, actually gave the compound $[Ba_5(O)(tmhd)_5(Htmhd)_4(OH)_3]$ as a final product, [50,51] with the formation of an oligomeric species to satisfy the metals coordinative saturation (Fig. 4). Indeed, the commercially available compound '$Ba(tmhd)_2$' is in fact likely to be this hydrated oligomeric material. The inclusion of water has caused numerous problems when the material is utilized as a MOCVD precursor, including higher than normal sublimation temperatures, poor volatility (mass transport), and high residues (due to the decomposition of the material before sublimation) [48,56].

If reactions of this type are carried out in rigorously non-aqueous media (e.g. utilizing the metal with Htmhd in dry pentane) and under anaerobic conditions in the presence of a mono or bidentate Lewis base (e.g. Et_2O, [57] MeOH, [58–60] bipy, [61] NH_3, [62] *o*-phen, [63]), then it is possible to obtain products with good purities and without water contaminants. The presence of the aforementioned Lewis bases have been shown, by X-ray structural analysis, to give rise to discrete dimeric molecules (e.g. Fig. 5).

Similarly, if a multidentate Lewis base is utilized (with at least four possible binding sites for the heavier metals), the oligomerization seen above in Fig. 4 may be further reduced to give monomeric species of the form $[M(tmhd)_2(L)]$ (where M, Sr; and Ba; L, triglyme; tetraglyme; Fig. 6 shows the structure of one of these molecules) [64–71].

If the multidentate Lewis base (glyme) ligand utilized contains three oxygens, dimeric compounds may be observed, e.g. $[Ba(tmhd)_2(di)]_2$ (made under anaerobic conditions, Fig. 7) and $[Sr(tmhd)_2(di)(\mu\text{-}H_2O)]_2$ (formed via the fortuitous incorporation of water into the anhydrous complex) [72–75].

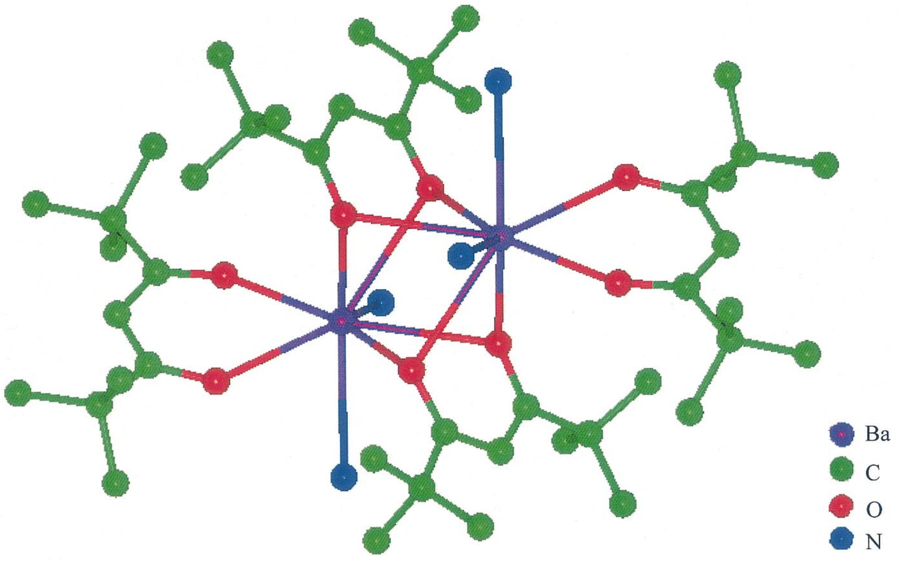


Fig. 5

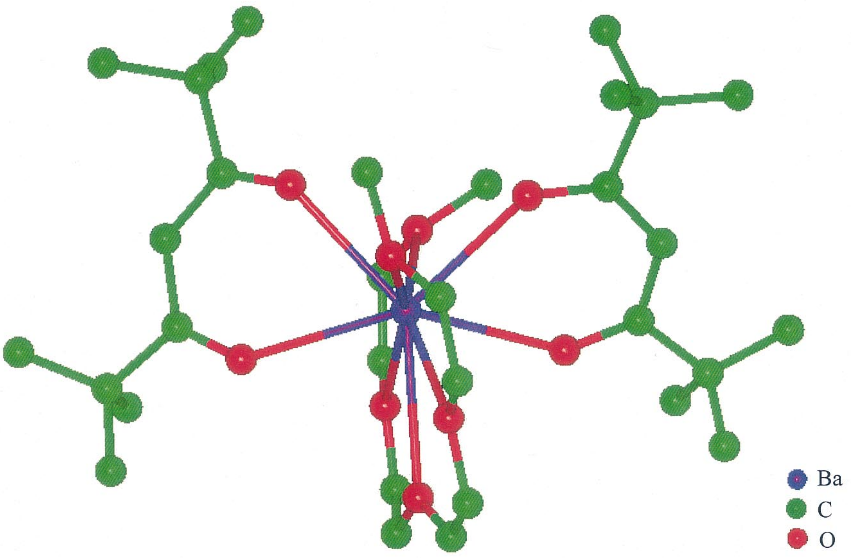


Fig. 6

Fig. 5. Molecular structure of the centrosymmetric dimer $[Ba(tmhd)_2(NH_3)_2]_2$ [62]. Each barium center is eight coordinate.

Fig. 6. Molecular structure of $[Ba(tmhd)_2(tet)]$ [70,71]. The barium center is nine coordinate with a geometry best described as a distorted dodecahedron with an additional oxygen intruding on one edge.

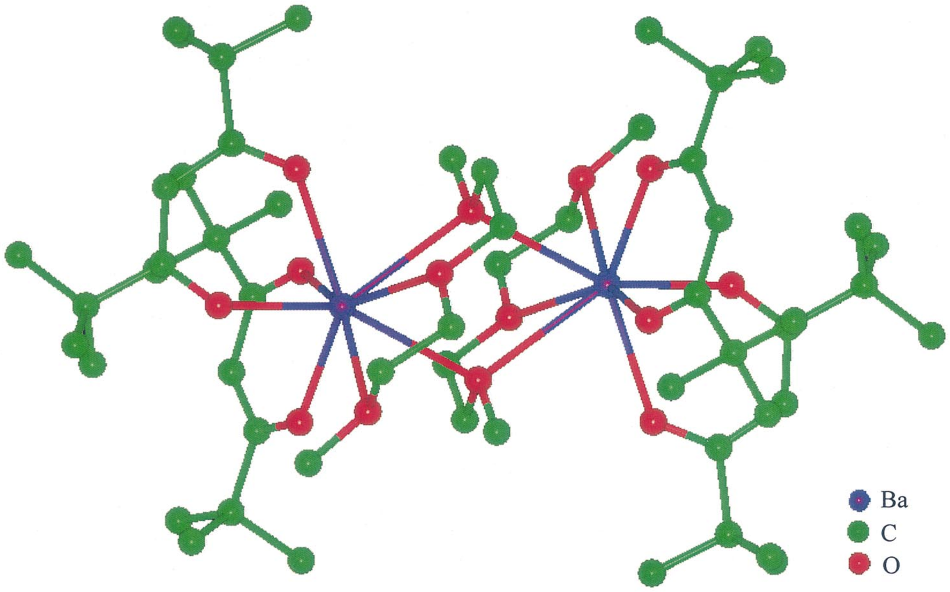


Fig. 7

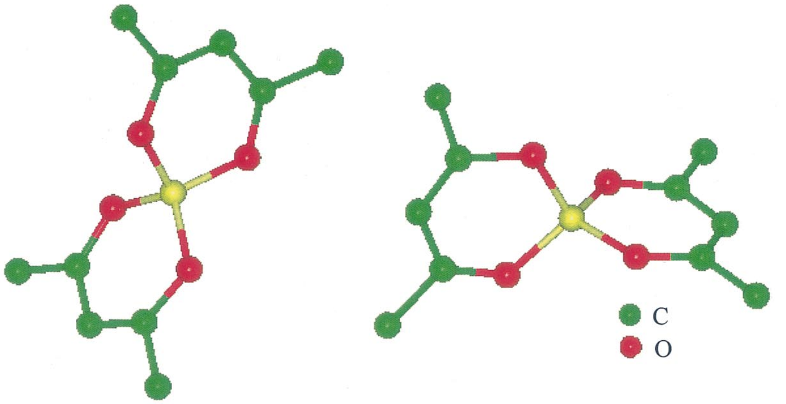


Fig. 8

Fig. 7. Molecular structure of the centrosymmetric dimer $[Ba(tmhd)_2(di)]_2$. Each barium center is eight coordinate with a distorted square antiprismatic geometry [74,75].
Fig. 8. Molecular structure of $Be(acac)_2$.

These glyme based complexes may be synthesized via addition of a glyme ligand to one of the homoleptic, anhydrous β-diketonate complexes described later in this chapter under anaerobic conditions or, as shown more recently, via a water based route [76]. The latter reaction proceeds with the total removal of any coordinated water for the triglyme and tetraglyme based compounds, but any water present is retained in the case of diglyme complexes.

If on the other hand, the reactions are worked up in the absence of any Lewis base, via either an ethoxide starting material or by utilizing liquid ammonia as a reactant, then true homoleptic species may be isolated, e.g. for calcium the trimer $[Ca(tmhd)_2]_3$ [77] is obtained and for barium, the tetramer $[Ba(tmhd)_2]_4$ [2,3]. Thus, it may be seen that quite often the final reaction products are dependent on the methodology utilized during synthesis. Those compounds that have been studied crystallographically are illustrated in the figures herein and in Tables 1–3, 6 and 8. Physical data for the known Group 2 element β-diketonate complexes may be found in Tables 4, 5, 7 and 9.

8. Beryllium

There are only a few Be β-diketonate complexes described in the literature (see Table 1). Of these, the most studied complex is the $acac^-$ derivative. The synthesis of $Be(acac)_2$ is accomplished by the reaction of $BeCl_2$ and Hacac in aqueous alcohol [78,79]. The compound is a simple monomer in both the solid and gaseous states as shown by X-ray diffraction and Gas Phase Electron Diffraction (GPED; Fig. 8).

9. Magnesium and calcium

Crystallographic data for magnesium and calcium β-diketonate complexes may be found in Tables 2 and 3, respectively. Physical characteristics are presented in Tables 4 and 5. The magnesium and calcium 2,4-pentanedionate derivatives, $[Mg(acac)_2(H_2O)_2]$ [80] and $[\{Ca(acac)_2(H_2O)_2\} \cdot H_2O]_\infty$ [85] (Fig. 9 a and b) are both monomeric, but the calcium compound as a result of a lattice water molecule is involved in extensive hydrogen bonding.

In contrast, the Lewis base free derivative was isolated by dehydration of the hydrated complex and was found to be a trimer $[Mg_3(acac)_6]$ (Fig. 10) [82]. The terminal magnesium ions are tris-chelated in a propeller-like fashion, while the central magnesium ion is surrounded by six bridging β-diketonate oxygen atoms. The molecule can be viewed as $[Mg\{Mg_2(acac)_6\}]$.

Hollander and co-workers in the early 1970's described a series of diphenyl-1,3-propanedionate compounds of magnesium, [83] and calcium [88] as Lewis base adducts, e.g. $[Mg(dppd)_2(dmf)_2]$ [83] (Fig. 11), and $[Ca_4(dppd)_8(EtOH)_2]$ [99]. Also recently Rees et al. [150] have synthesized and characterized $[Mg(tmhd)_2(Et_2O)_2]$.

The magnesium in both compounds is octahedrally coordinated to the oxygen atoms of two DMF molecules and two β-diketonate ligands. In contrast, the calcium derivative is a tetramer, with two six coordinate and two seven coordinate calcium ions. The structure consists of an O_8 cube with the calcium ions μ_4-capping at four cube faces. The authors observed the ability of the heavier Group 2 metals, calcium and strontium, to accommodate coordination numbers greater than six, whilst magnesium is restricted to an octahedral geometry.

Table 1
Beryllium β-diketonate compounds[a]

Compound	Space group	a/Å, α/°	b/Å, β/°	c/Å γ/°	Average M–O (β-diket)/Å	References
$[Be(acac)_2]$	$P2_1$	13.537(2) –	11.378(2) 100.76(1)	7.762(1) –	1.625	[78]
$[Be(acac)_2]$ (GPED)	D_2d	–	–	–	1.615	[79]

[a] –Line indicates data that was not reported in the literature, or is otherwise not relevant to the compound described.

Fig. 8. Molecular structure of $Be(acac)_2$.

Table 2
Magnesium β-diketonate compounds[a]

Compound	Space group	a/Å, α/°	b/Å, β/°	c/Å, γ/°	Average M–O (β-diket)/Å	Average M–O (L)/Å	References
$[Mg(acac)_2(H_2O)_2]$	$P2/c$	10.983 (1) –	5.354 (1) 106.36(14)	11.176 (1) –	2.034	2.148 (H_2O) –	[80]
$[Mg(acac)Cl(H_2O)_2]_2$ $[Mg(acac)_2(H_2O)_2]$	$P2_1/c$	7.835(2) –	18.164(4) 90.70(2)	13.303(3) –	2.093	2.491 (Cl) 2.037 (H_2O)	[81]
$[Mg(acac)_2]_3$	P-1	8.749(6)	10.958(6)	11.173(9)	2.082	–	[82]
$[Mg(dppd)_2(dmf)_2]$	C_2/c	16.893(3) –	12.853(2) 117.08(5)	16.927(3) –	2.056	2.095 (dmf) –	[83]
$[C_{14}H_{19}N_2]^{+}\mathrm{lMg(hfac)_3]^{-}}$	$P2_1/n$	12.775	21.268	13.594	2.06	–	[84]

[a] –Line indicates data that was not reported in the literature, or is otherwise not relevant to the compound described.

Table 3
Calcium β-diketonate compounds[a]

Compound	Space group	a/Å, α/°	b/Å, β/°	c/Å, γ/°	Average M–O (β-diket)/Å	Average M–O (L)/Å	References
$[Ca(acac)_2(H_2O)] \cdot H_2O$	*Pbnb*	5.260 (2)	13.683 (3)	20.062 (7)	2.328	2.356 (H_2O)	[85]
		–	–	–			
$[Ca(dppd)_2(EtOH)_{0.5}]_4$	*P*-1	15.247 (1)	13.555 (1)	14.097 (1)	2.365	2.408 (EtOH)	[86]
			74.64 (1)	95.97 (1)		113.59 (1)	
$[Ca(dppd)_2(pmdeta)]$	C_2/c	50.531 (7)	17.625 (5)	12.230 (3)	2.317	2.633 (pmdeta)	[87]
		–	101.84 (1)	–			
$[Ca(dppd)_2(Hdppd)]$	*P*-1	9.775 (3)	10.620 (3)	17.811 (2)	1.874	–	[87]
		92.77 (1)	94.75 (1)	107.14			
$[Ca_3(tmhd)_6]$	$Pca2_1$	20.023 (4)	19.638 (6)	18.906 (5)	2.372	–	[77]
$[Ca(tmhd)_2(EtOH)]_2$	*P*-1	13.556 (6)	14.138 (6)	23.266 (9)	2.337	2.35	[77]
		74.07 (2)	73.96 (2)	80.25 (3)			
$[Ca(tmhd)_2(tri)]$	*P*-1	10.378 (3)	11.601 (4)	15.483 (3)	2.362	2.534 (tri)	[88]
		84.03 (3)	71.75 (2)	82.61 (3)			
$[Ca(tmhd)(OEt)(EtOH)]_4$	$P2_1/c$	14.781 (2)	26.959 (7)	20.443 (2)	2.310 (Oph)	2.347 (OEt)	[89]
		–	110.60 (2)	–		2.404 (EtOH)	
$[Ca(tmhd)(OPh)(MeOH)]_4$	*P*-1	12.758 (6)	15.460 (7)	24.862 (14)		61 (MeOH)	
		101.41 (4)	91.71 (4)	101.84 (4)			
$[Ca(tmhd)(OAr_N)(EtOH)]_2$	*P*-1	10.222 (8)	13.925 (11)	22.331 (2)		2.730 (N, EtOH)	[91]
		98.11 (12)	97.80 (5)	96.10 (7)			
$[Ca_2(tmhd)_3$-$(OCH_2CH_2Nme_2)]_2$	$P2_1/c$	14.180 (1)	12.047 (3)	25.114 (5)	2.322	2.354 (OR)	[89]
		–	100.64 (1)	–		2.519 (N)	
$[Ca(fod)_2(tri)]$	$P2/n$	11.894 (9)	10.699 (6)	14.837 (8)	2.365	2.503 (tri)	[92]
$[Ca(hfac)_2(H_2O)_2]_2$	*P*-1	11.205 (1)	9.838 (1)	9.095 (1)	2.418	2.387 (H_2O)	[93]
		–	96.19 (1)	–			
$[Ca(hfac)_2(tet)]$	*P*-1	9.453 (2)	12.600 (2)	13.215 (4)	2.402	2.468 (tet)	[88]
		70.30 (2)	83.09 (2)	76.49 (2)			
$[\{Ca(hfac)_2\}_2(hept)]$	$P2_1/c$	10.288 (2)	24.335 (5)	11.011 (2)	2.390	2.497 (hept)	[94]
		–	109.66 (12)	–			

[a] –Line indicates data that was not reported in the literature, or is otherwise not relevant to the compound described.

Table 4
Physical data for magnesium β-diketonate compounds[a]

Compound	Melting point (°C)	Sublimation temperature (°C)	Solubility, e, ar, alk	Thermal data (°C)	Other	References
$[\mathrm{Mg(acac)_2(H_2O)_2}]$	–	–	–	–	–	[80]
$[\mathrm{Mg(acac)Cl(H_2O)_2}]_2$	–	–	–	–	–	[81]
$[\mathrm{Mg(acac)_2(H_2O)_2}]$	–	–	–	–	–	
$[\mathrm{Mg(acac)_2}]_3$	–	–	–	–	–	[82]
$[\mathrm{Mg(acac)_2(EtOH)_2}]n$	Dec 258–261	–	s, sls, ns	–	Ms	[90]
$[\mathrm{Mg(dppd)_2}]n$	Dec 202–206	–	s, s, ns	–	Ms	[90]
$[\mathrm{Mg(dppd)_2(dmf)_2}]$	–	–	–	–	–	[83]
$[\mathrm{C_{14}H_{19}N_2}]^{+}\mathrm{lMg(hfac)_3}]^{-}$	–	–	–	–	–	[84]
$[\mathrm{Mg(hfac)_2(EtOH)_2}]n$	Dec 175–177	–	s, s, ns	–	Ms	[90]
$[\mathrm{Mg(Oet)(hfac)(EtOH}]n$	135–137	–	s, s, sls	–	Ms	[90]
$[\mathrm{Mg(hfac)_2(dme)}]n$	55–61	–	s, s, sls	–	Ms	[90]
$[\mathrm{Mg(hfac)_2(hept)_{0\cdot5}}]n$	Liquid	–	s, s, sls	–	Ms	[90]
$[\mathrm{Mg(fod)_2(EtOH)_{0.5}}]n$	Liquid	–	s, s, sls	–	Ms	[90]
$[\mathrm{Mg(fod)_2(tri)_{0.5}}]n$	126–129	–	s, s, sls	–	Ms	[90]
$[\mathrm{Mg(tmhd)_2}]\mathrm{n}$	258–261	140–165	s, s, s	Sublimes intact	Ms	[90]
$[\mathrm{Mg(tmhd)_2(EtOH)_{0.5}}]n$	83–85	–	s, s, s	–	Ms	[90]
$[\mathrm{Mg(tmhd)_2(di)_{0.5}}]n$	104–107	–	s, s, s	–	Ms	[90]
$[\mathrm{Mg(tmhd)_2(tri)_{0.5}}]n$	120–123	–	s, s, s	Losses L, then sublimation	Ms	[90]

[a] –Line indicates data that was not reported in the literature, or is otherwise not relevant to the compound described; dec, decomposes; des, desolvates e, ethers (such as thf, $\mathrm{Et_2O}$); ar, aromatic solvents such as toluene or benzene; and alk, alkanes (hydrocarbons) such as n-hexane or n-heptane; sublimatio temperatures are at 10^{-2} Torr or lower (reduced pressure); thermal data is at 1 atm.; subl, sublimes; L, adduct ligand; ms, mass spectrum reported; dep deposition reported with compound data; vp, vapor pressure reported; where a_n is shown in the compound formula, it is denoting that the exact solid stat formulation is not known (i.e. whether the compound is a monomer, dimer etc).

Table 5
Physical data for calcium β-diketonate compounds[a]

Compound	Melting point (°C)	Sublimation temperature (°C)	Solubility, e, ar, alk	Thermal data (°C)	Other	References
$[Ca(acac)_2(H_2O)]\cdot H_2O$	–	–	–	–		[85]
$[Ca(acac)_2(EtOH)_2]_n$	Dec 267–269	–	s, sls, ns	–	Ms	[90]
$[Ca(dppd)_2]_n$	Dec 267–270	–	s, s, ns	–	Ms	[90]
$[Ca(dppd)_2(EtOH)_{0.5}]_4$	274	–	–	–	–	[86]
$[Ca(dppd)_2(pmdeta)]$	143–145	–	s, s, ns	–	Ms, air stable	[87]
$[Ca(dppd)_2(Hdppd)]$	68–72	–	s, s, ns	Two step subl 230–411	Ms	[87]
$[Ca(dmppd)_2]_n$	Dec	–	–	–	–	[49]
$[Ca(tfac)_2]_n$	Dec 170–255	190–200	s, s, ns	–	Ms, dep	[95]
$[Ca(hfac)_2]_n$	Dec 170–230	130–150	s, s ns	–	Ms, dep	[95]
$[Ca(hfac)_2(H_2O)_2]_2$	–	–	–	–		[93]
$[Ca(hfac)_2(EtOH)_{0.5}]n$	Dec 180–183	–	s, s, ns	–	Ms	[90]
$[Ca(hfac)_2(tri)]_n$	103–106	–	s, s, s	–	Ms	[87]
$[Ca(hfac)_2(tet)]$	82–85	130–150	s, s, s	Sublimes intact	Ms	[88]
$[\{Ca(hfac)_2\}_2(hept)]$	112–116	–	s, s, s	Sublimes intact no temperature given	Ms	[94]
$[Ca(hfac)_4]_2(pmdetaH)$	83–86	–	s, s, ns	–	Ms	[87]
$[Ca(hfac)_2(18\text{–}C\text{–}6)]_n$	–	–	–	–	NMR	[96]
$[Ca(hfac)_2(2N\text{-}18\text{–}C\text{-}6)]_n$	–	–	–	–	NMR	[96]
$[Ca(fod)_2]_n$	201–205 s	–	s, ns, s	–	Ms	[90]
$[Ca(fod)_2(tri)]$	80–83	–	s, s, s	–	Ms	[92]
$[Ca_3(tmhd)_6]$	238–241	170–220	s, s, s	Sublimes intact	Ms, dep	[25,77]
$[Ca(tmhd)_2(EtOH)]_2$	Des 112–115, melt 235–238	–	s, s, s	Losses L, then subl	Ms	[77]
$[Ca(tmhd)_2(tri)]$	71–74	–	s, s, s	Losses L, then subl	Ms, air stable	[88]
$[Ca(tmhd)_2(tet)]_n$	50–55	–	s, s, s	–	Ms	[90]
$[Ca(tmhd)_2(hept)_{0.5}]_n$	82–87	–	s, s, s	–	Ms	[90]
$[Ca(tmhd)_2(tmeda)]_n$	117–119	–	s, s, s	–	Ms, air stable	[87]
$[Ca(tmhd)(OEt)(EtOH)]_4$	Des 67	170–200 minimal	s, s, sls	–	Ms	[89]
$[Ca(tmhd)(OPh)(MeOH)]_4$	Des 139–143	–	s, s, sls	–	Ms	[90]
$[Ca(tmhd)(OArN)(EtOH)]_2$	Des 145–150, melt 219–224	–	s, s, sls	–	Ms	[90]

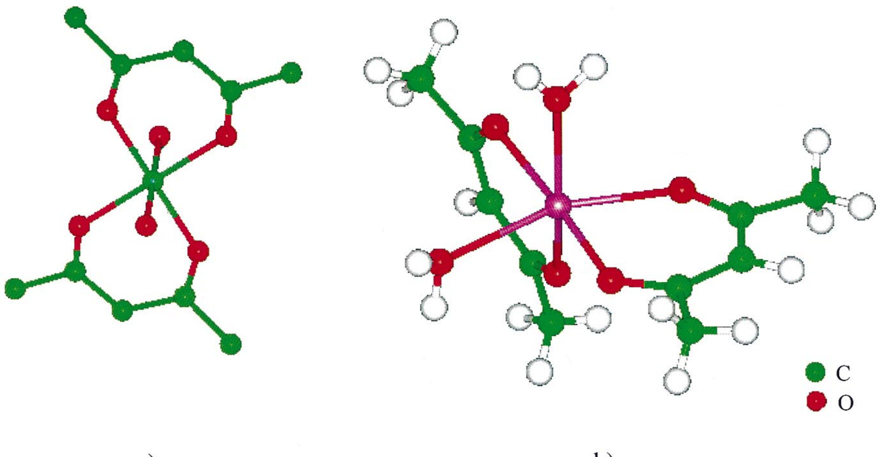
Table 5 (*Continued*)

Compound	Melting point (°C)	Sublimation temperature (°C)	Solubility, e, ar, alk	Thermal data (°C)	Other	References
$[Ca(tmhd)_{1.5}(OAr_N)_{0.5}]_n$	219–225	–	s, s, sls	–	Ms	[90]
$[Ca_2(tmhd)_3(OCH_2CH_2NMe_2)]_2$	>280	Minimal	s, s, sls	–	Ms	[89]
$[Ca(tmhd)_{1.5}(OCH_2CH_2OPr^i)_{0.5}]_n$	Dec 280	–	s, s, sls	–	Ms	[90]

[a] –Line indicates data that was not reported in the literature, or is otherwise not relevant to the compound described; dec, decomposes; des, desolvates e, ethers (such as thf, Et_2O); ar, aromatic solvents such as toluene or benzene; and alk, alkanes (hydrocarbons) such as n-hexane or n-heptane; sublimation temperatures are at 10^{-2} Torr or lower (reduced pressure); thermal data is at 1 atm.; subl, sublimes; L, adduct ligand; ms, mass spectrum reported; dep deposition reported with compound data; vp, vapor pressure reported; where a_n is shown in the compound formula, it is denoting that the exact solid stat formulation is not known (i.e. whether the compound is a monomer, dimer etc).

Interestingly, several workers [97,98] have suggested that an improvement is seen in the volatilities of the β-diketonate compounds in the MOCVD apparatus when free β-diketone is added to the carrier gas, resulting from a decrease in the degree of aggregation.

This observation was clearly demonstrated when a tris-substituted derivative was isolated as the monomer, [Ca(dppd)$_2$(Hdppd)] (Fig. 12); [87] significantly the bis-substituted compound is an oligomer (tetrameric or larger).



a) b)

Fig. 9

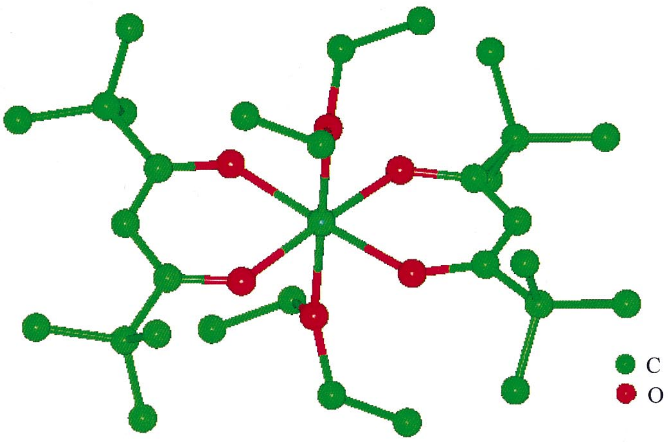


Fig. 11

Fig. 9. (a) Molecular structure of [Mg(acac)$_2$(H$_2$O)$_2$] [80] and (b) crystal structure of [{Ca(acac)$_2$(H$_2$O)$_2$} · H$_2$O]$_\infty$ [85].

Fig. 11. Molecular structure of [Mg(dppd)$_2$(dmf)$_2$] [83].

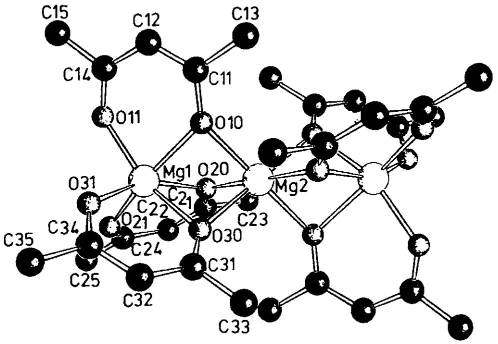


Fig. 10. Molecular structure of [$Mg_3(acac)_6$] [82].

The calcium is six coordinate with three chelating dppd ligands arranged in a distorted octahedral geometry. The methylene proton is disordered over all three ligands resulting in near identical Ca–O, C–O and C–C bond lengths and angles.

The stabilization of the dppd derivative as a monomer [$Ca(dppd)_2(pmdeta)$] with a tridentate amine (pmdeta) ligand has also been achieved (Fig. 13) [87].

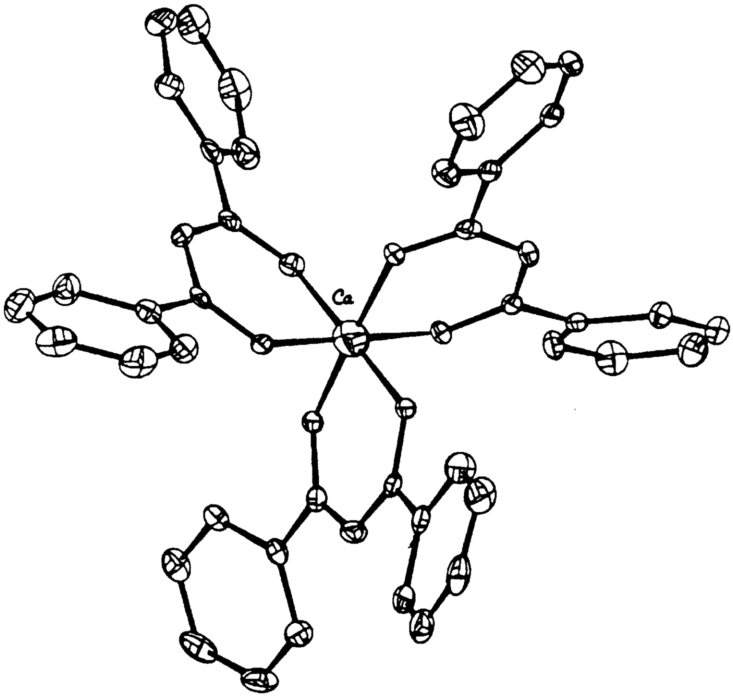


Fig. 12. Molecular structure of [$Ca(dppd)_2(Hdppd)$] [87].

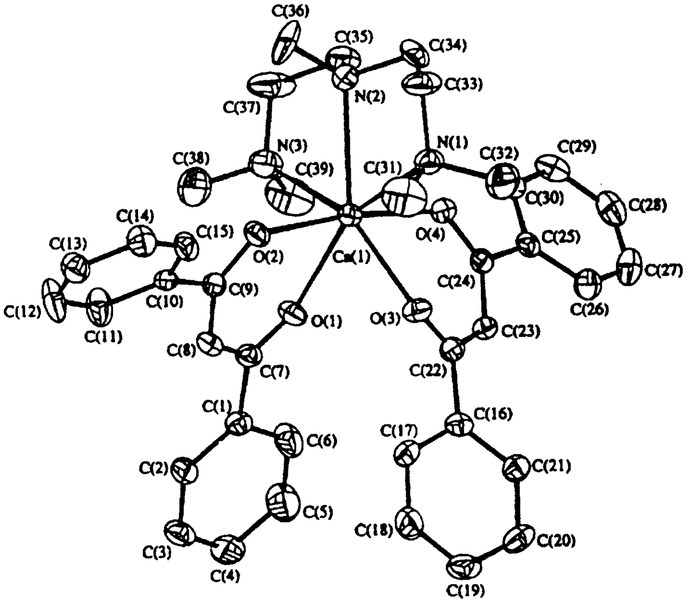


Fig. 13. Molecular structure of [Ca(dppd)$_2$(pmdeta)] [87].

The calcium ion is seven coordinate and has a distorted capped octahedral geometry. The tridentate amine ligand and the two dppd ligands lie in different planes to produce a twisted propellane structure.

The poor volatility behavior of Group 2 element 2,4-pentanedionates and diphenyl-1,3-propanedionates led researchers to investigate the physico-chemical properties of the fluoro-substituted and sterically bulky β-diketonate ligands, e.g. hfac, fod and tmhd.

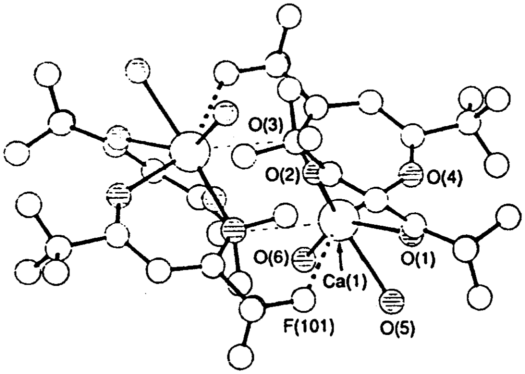


Fig. 14. Molecular structure of [Ca$_2$(hfac)$_4$(H$_2$O)$_4$] [93].

Recently, Bradley et al. [93] reported the structural characterization of the hydrated dimer [$Ca_2(hfac)_4(H_2O)_4$] (Fig. 14). The calcium ions are eight coordinate and lie in a distorted dodecahedral geometry. The coordination sphere consists of a chelating hfac ligand, two water molecules, a second chelating hfac ligand which also bridges the two calcium ions through one of the oxygen atoms and a Ca–F interaction via a CF_3 group on a neighboring hfac ligand.

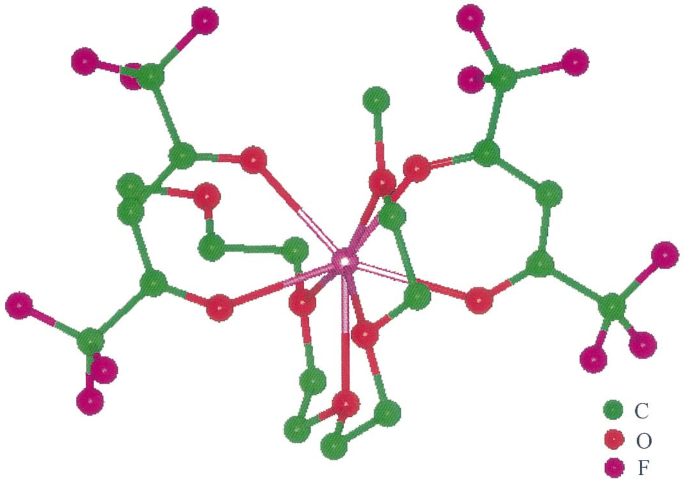


Fig. 15

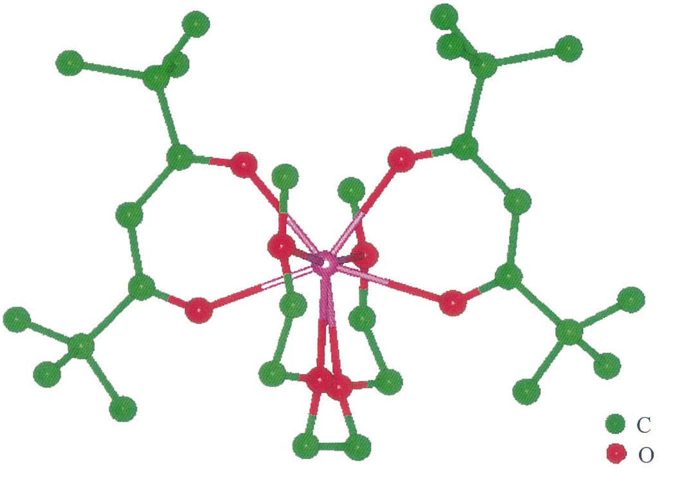


Fig. 16

Fig. 15. Molecular structure of [$Ca(hfac)_2(tet)$] [88].
Fig. 16. Molecular structure of [$Ca(tmhd)_2(tri)$] [88].

Interestingly, the molecular architecture of this compound may be modified by adding a multidentate Lewis base, which will effectively ‘plug’ the vacant coordination sites on the metal and restrict any bridging interactions. Thus, by employing a glyme ligand such as tetraglyme, an eight coordinate monomeric compound has been isolated [$Ca(hfac)_2(tet)$] [88] (Fig. 15).

The calcium ion is bonded to two chelating hfac ligands and to four oxygen atoms of the tetraglyme ligand in a distorted square antiprismatic geometry. Surprisingly, despite the apparent space around the calcium center, the fifth glyme oxygen atom does not participate in bonding. Thus, it would seem that calcium prefers to adopt an eight rather than a possible nine coordinate geometry.

In contrast, the related magnesium derivative is isolated as a tris-substituted anionic compound $[Mg(hfac)_3]^-$ stabilized by a protonated 1,8-bis-(dimethylamino)naphthalene molecule [84]. The magnesium is six coordinate with six oxygen atoms of the three chelating hfac ligands. Although the reaction mechanism is unclear, it is suggested that proton transfer onto the amine ligand initiates formation of the tris-substituted anion, similar observations were noted for the reactions of fluoro-substituted β-diketonate complexes $[Sr(tfac)_4]^{2-}$ [87] and $[Ba(hfac)_5]^{3-}$ [50,51], which were stabilized by protonated tmeda and ethylenediamine ligands, respectively.

Another representative of the fluoro-substituted β-diketonates is the heptafluoro derivative [$Ca(fod)_2(tri)$] [92]. The gross molecular structure is very similar to that of the tmhd derivative [$Ca(tmhd)_2(tri)$] [88] (Fig. 16). The calcium ion is eight coordinate and the coordination polyhedron may be considered as a distorted square antiprismatic. In this compound the triglyme ligand is observed to be lying in a meridional plane, whilst the two tmhd groups are lying, respectively, above and below the plane in an approximately orthogonal relationship.

A comprehensive study by Arunasalam [77,89,90] of the formation and reactions of some magnesium and calcium β-diketonate compounds has been undertaken.

One of the most interesting results of this study was the isolation of the homoleptic calcium tmhd compound [$Ca_3(tmhd)_6$] in good purity and yield (Fig. 17). This compound may be readily utilized in the MOCVD of CaO containing materials [25].

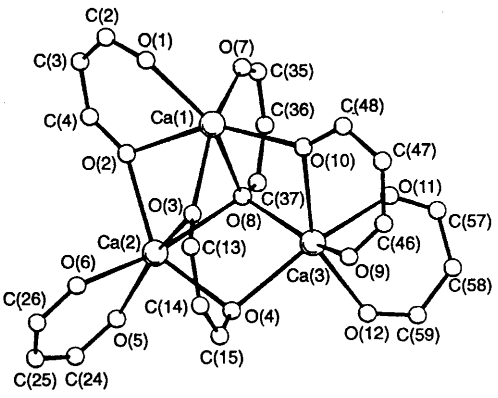


Fig. 17. Molecular structure of [$Ca_3(tmhd)_6$] [77].

Table 6
Strontium β-diketonate compounds[a]

Compound	Space group	a/Å, α/°	b/Å, β/°	c/Å, γ/°	Average M–O (β-diket)/Å	Average M–O (L)/Å	References
$[Sr(dppd)_2(Me_2CO)]_4$	*P*-1	13.759 (50) 107.57 (3)	14.182 (10) 90.36 (20)	16.031 (20) 113.07 (20)	2.500	2.600 (Me_2CO)	[99]
$[Sr(dppd)_2(tet)]$	*P*2_1/*c*	12.950 (2) –	27.008 (4) 112.55(3)	12.373 (7) –	2.540	2.748 (tet)	[73]
$[Sr(tfac)_4]_2[tmedaH]$	*Fdd*2	27.095 (4) –	28.416 (3) –	11.154 (1) –	2.571		[87]
$[Sr(hfac)_2(tri)(H_2O)]_2$	*P*-1	10.3889 (7) –	11.432 (7) 129.91 (11)	13.324 (1) –	2.572	2.718 (tri) 2.763 (H_2O)	[100,101]
$[Sr(hfac)_2(tri)]$	*C*2/*c*	22.916 (3) 114.20 (9)	9.337 (1) 95.87 (7)	16.414 (2) 101.94 (7)	2.521	2.651 (tri)	[100,101]
$[Sr(hfac)_2(tet)]$	*Pbca*	20.934 (2) –	17.820 (1) –	15.872 (4) –	2.548	2.713 (tet)	[100,101]
$[Sr(fod)_2(tri)]$	*P*2/*n*	[b]					[92]
$[Sr_3(tmhd)_6(Htmhd)]$	*P*-1	14.413 (4) 97.20 (1)	14.658 (5) 100.20 (2)	24.352 (9) 109.82 (2)	2.498	–	[44–47]
$[Sr(tmhd)_2(di)(H_2O)_{0.5}]_2$	*C*2/*c*	29.267 (6)	10.565 (2) 95.99 (1)	21.846 (5) –	2.489	2.681 (di) 2.967 (H_2O)	[72]
$[Sr(tmhd)_2(tri)]$	*P*2_1/*c*	11.986 (5) –	19.705 (3) 96.24 (2)	15.490 (2) –	2.495	2.674 (tri)	[72]
$[Sr(tmhd)(OSiPh_3)]_3$	*P*-1	13.62 96.66	13.82 93.1	25.472 115.1	2.491	2.521 ($OSiPh_3$)	[102]

[a] –Line indicates data that was not reported in the literature, or is otherwise not relevant to the compound described.
[b] Isostructural with $[Ca(fod)_2(tri)]$; parameters not determined.

Table 7
Physical data for strontium β-diketonate compounds[a]

Compound	Melting point (°C)	Sublimation temperature (°C)	Solubility, e, ar, alk	Thermal data (°C)	Other	References
$[Sr(acac)_2(EtOH)]_n$	Dec 180	–	sls, ns, ns	Five step dec	Ms	[103]
$[Sr(dppd)_2(EtOH)]_n$	Dec 210	–	sls, ns, ns	Four step dec	Ms	[103]
$[Sr(dppd)_2(Me_2CO)]$	–	–	–	–		[99]
$[Sr(dppd)_2(tet)]$	96–98	–	s, s, sls	–	Ms	[73]
$[Sr(tfac)_2]_n$	Dec 160–230	200–225	s, –, –	–	Ms, dep	[95]
$[Sr(tfac)_2(tri)]_n$	73–75	–	s, s, sls	–	Ms	[73]
$[Sr(tfac)_4]_2(tmedaH)$	86–88	–	s, s, ns	–	Ms	[87]
$[Sr(tfac)_4]_2(pmdetaH)$	98–102	–	s, s, ns	–	Ms	[87]
$[Sr(tfac)_4]_2(hmtetaH)$	69–72	–	s, s, ns	–	Ms	[87]
$[Sr(hfac)_2]_n$	Dec 220–275	180–190	s, –, –	–	Ms, dep	[95]
$[Sr(hfac)_2(EtOH)]_n$	Des 106	150–170	s, sls, ns	Two step subl	Ms	[103]
$[Sr(hfac)_2(tri)(H_2O)]_2$	Dec 210	–	s, sls, ns	–	Ms	[100,101]
$[Sr(hfac)_2(tri)]$	84–86	160–180	s, s, s	Subl intact	Ms	[100,101]
$[Sr(hfac)_2(tet)]$	93–95	150–170	s, s, s	Subl intact	Ms	[100,101]
$[Sr(hfac)_2(18\text{-}C\text{-}6)]_n$	–	–	–	–	NMR	[96]
$[Sr(hfac)_2(2N\text{-}18\text{–}C\text{-}6)]_n$	–	–	–	–	NMR	[96]
$[Sr(fod)_2(tri)]$	86–88	–	s, s, s	–	Ms	[92]
$[Sr_3\ (tmhd)_6(Htmhd)]$	172–176	180–210	s, s, s	Two step subl	Ms, low T NMR	[44–47]
$[Sr(tmhd)_2(di)(H_2O)_{0.5}]_2$	96–98	–	s, s, sls	–	Ms	[72]
$[Sr(tmhd)_2(tri)]$	87–89	–	s, s, s	Loss of L, then subl	Ms	[72]
$[Sr(tmhd)_2(tet)]_n$	56–60	–	s, s, s	Loss of L, then subl	Ms	[87]
$[Sr(tmhd)(OSiPh_3)]_3$	195–198	–	s, s, sls	Multi step dec	Ms	[102]
$[Sr(tmhd)(OEt)(EtOH)_{0.66}]_n$	Des 72	–	s, sls, ns	Three step dec	Ms, low T NMR	[89]
$[Sr(tmhd)(OCH_2CH_2NMe_2)]_n$	Des 72	–	s, s, sls	Four step dec	Ms	[103]
$[H_{0.5}Sr(tmhd)_{1.5}(OCH_2CH_2OMe)]_n$	Dec 170	–	s, s, sls	Two step dec	Ms	[89]
$[H_{0.5}Sr(tmhd)_{1.5}(OCH_2CH_2N(Me)CH_2CH_2NMe_2)]_n$	135–138	–	s, s, s	Three step dec	Ms	[103]
$[Sr(tmhd)(acac)(MeOH)_{1.33}]_n$	Dec 160	–	s, sls, ns	Three step dec	Ms	[103]
$[Sr(tmhd)(hfac)(EtOH)_{0.5}]_n$	98–102	–	s, s, sls	Three step dec	Ms, low TNMR	[103]

[a] –Line indicates data that was not reported in the literature, or is otherwise not relevant to the compound described; dec, decomposes; des, desolvates e, ethers (such as thf, Et_2O); ar, aromatic solvents such as toluene or benzene; and alk, alkanes (hydrocarbons) such as n-hexane or n-heptane; sublimatio temperatures are at 10^{-2} Torr or lower (reduced pressure); thermal data is at 1 atm.; subl, sublimes; L, adduct ligand; ms, mass spectrum reported; dep deposition reported with compound data; vp, vapor pressure reported; where a_n is shown in the compound formula, it is denoting that the exact solid stat formulation is not known (i.e. whether the compound is a monomer, dimer etc).

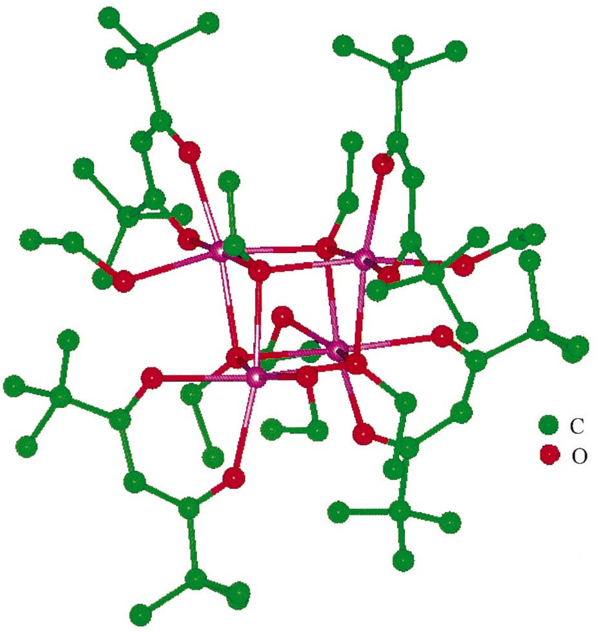


Fig. 18

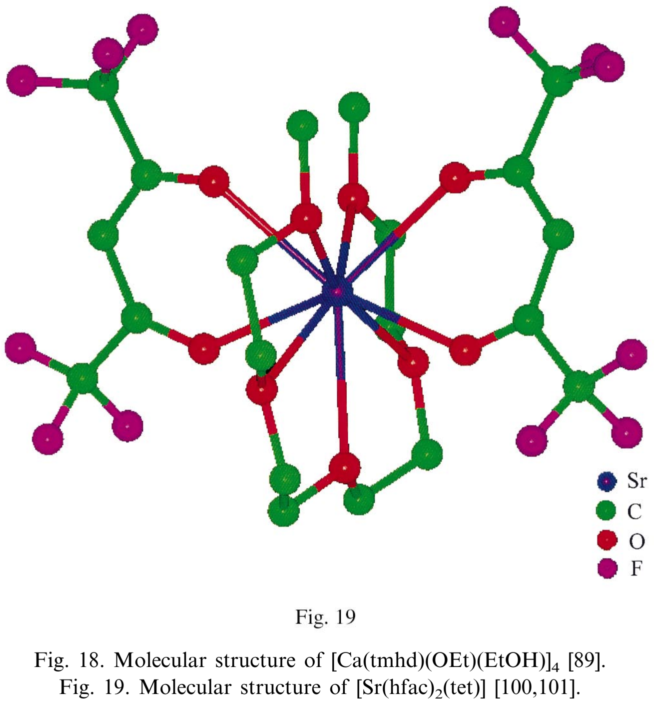


Fig. 19

Fig. 18. Molecular structure of [Ca(tmhd)(OEt)(EtOH)]$_4$ [89].
Fig. 19. Molecular structure of [Sr(hfac)$_2$(tet)] [100,101].

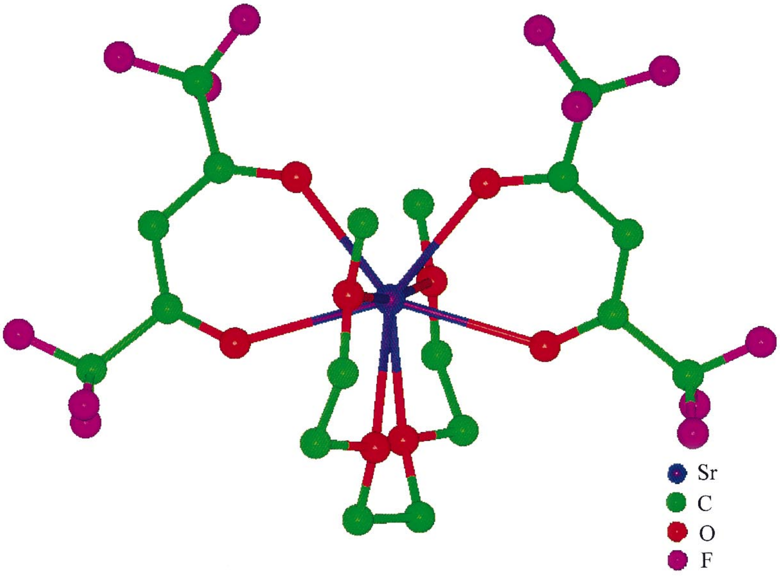


Fig. 20

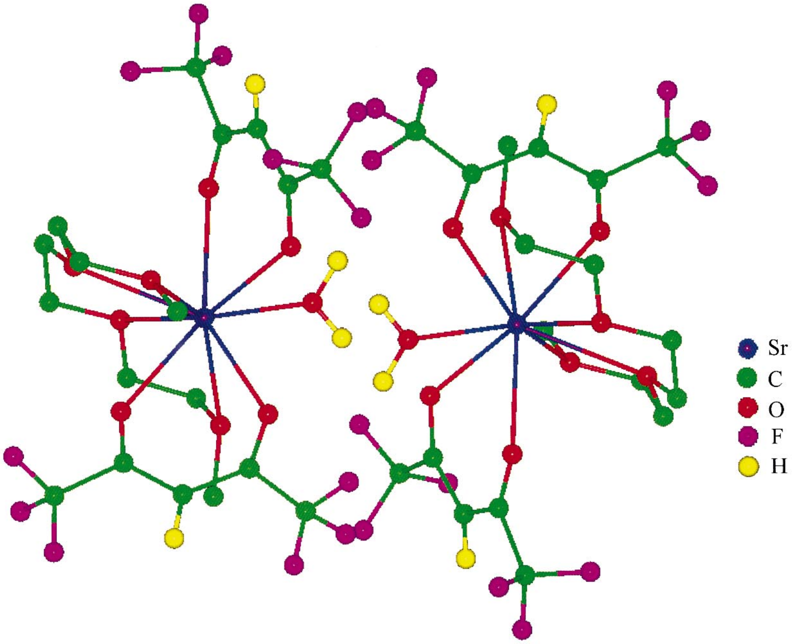


Fig. 21

Fig. 20. Molecular structure of [Sr(hfac)$_2$(tri)] [100,101].
Fig. 21. Molecular structure of [Sr(hfac)$_2$(tri)(H$_2$O)]$_2$ [100,101].

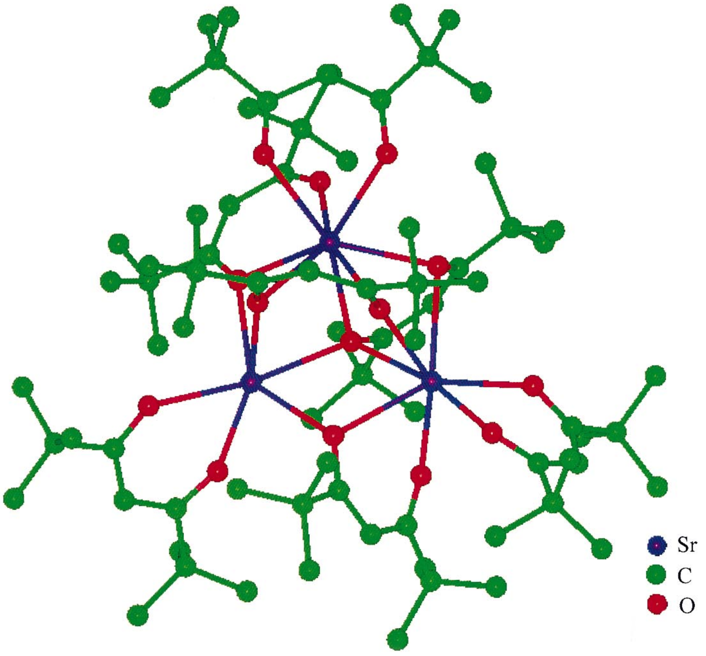


Fig. 22

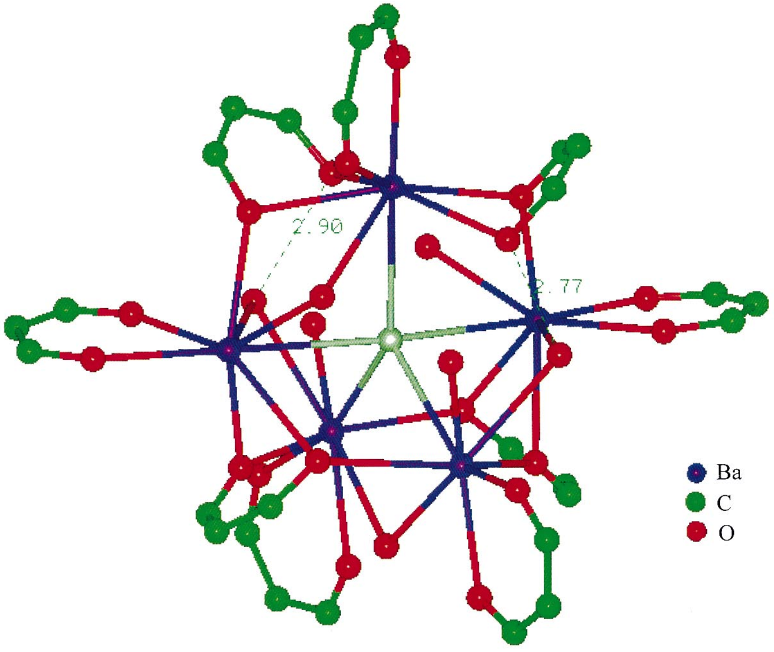


Fig. 23

Fig. 22. Molecular structure of $[Sr_3(tmhd)_6(Htmhd)]$ [44–47].
Fig. 23. Molecular structure of $[Ba_5(tmhd)_9Cl(H_2O)_7]$ [132].

A number of mixed anionic ligand compounds have also been reported for calcium, [89,91] including the cubane $[Ca(tmhd)(OEt)(EtOH)]_4$ (Fig. 18). These are, in general, non-volatile crystalline solids; however it has been postulated that they may be of utility as sol–gel precursors to CaO containing materials because of the 'cross-linking' potential of the β-diketone and/or alkoxide ligands [89].

10. Strontium compounds

There are relatively few crystallographically characterized strontium β-diketonate complexes in the literature, and those known are listed in Table 6. A full listing of those compounds reported in the literature, with their physical characteristics, is shown in Table 7. Apart from $[Sr(dppd)_2(Me_2CO)]_4$, which was studied in the early 1970's, [99] all of the other known compounds have been isolated during the current decade. These compounds can be neatly divided into two groups, Lewis base adducted compounds and others. The adducts $[Sr(dppd)_2(tet)]$, [73] $[Sr(t\text{-}fac)_4]_2[tmedaH]$, [87] $[Sr(hfac)_2(tet)]$ (Fig. 19), [100,101] $[Sr(hfac)_2(tri)]$ (Fig. 20), [100,101] $[Sr(fod)_2(tri)]$, [92] $[Sr(tmhd)_2(tri)]$, [72] are all monomeric, eight or nine coordinate crystalline solids.

The two water containing compounds $[Sr(hfac)_2(tri)(H_2O)]_2$ (Fig. 21), [100,101] and $[Sr(tmhd)_2(di)(H_2O)_{0.5}]_2$ [72] are an example of how precisely this type of compound requires its coordination sphere to be fulfilled. Thus, it can be stated that, for strontium, a nine coordinate metal center is desirable for air and moisture stability.

The unadducted compounds, the CVD precursor $[Sr_3(tmhd)_6(Htmhd)]$ (Fig. 22), [44–47] and $[Sr(tmhd)(OSiPh_3)]_3$, [102] are both trimeric, with a similar, triangular arrayed strontium metal centered, structural motif.

11. Barium compounds

In stark contrast to strontium, a very large variety of barium β-diketonate compounds have been reported. This may, in part, be due to the requirement for a volatile barium source for utilization in MOCVD techniques. As noted earlier, $YBa_2Cu_3O_{7-x}$ (YBCO) thin films (deposited by MOCVD) are of great current interest, [16–24] and as such, the lack of a volatile, reproducible source of barium for these materials is a distinct 'stumbling-block'. There are many publications regarding the MOCVD of barium containing films (via the use of barium β-diketonate compounds), and the reader is directed to reviews of the area for concise details [16–24,104,105].

It can be seen from Tables 8 and 9 (crystallographic and physical data tables for barium β-diketonate compounds, respectively) that a wide range of ligands have been utilized, with varying degrees of success. Many of the compounds are polymeric and/or contain water. Thus the inclusion of a Lewis base adduct to

Table 8
Barium β-diketonate compounds[a]

Compound	Space group	a/Å, α/°	b/Å, β/°	c/Å, γ/°	Average M–O (β-diket)/Å	Average M–O (L)/Å	References
[Ba(tfac)$_2$(tet)]	*P*-1	9.566 (3) 93.01 (2)	16.400 (3) 91.70 (2)	15.230 (4) 109.63 (2)	2.691	2.867 (tet)	[70,71]
[Ba(tfac)$_2$(hmteta)]	*Pbca*	14.607 (7) –	17.155 (6) –	25.507 (9) –	2.677	2.983 (hmteta)	[106]
[Ba(pta)$_2$(H$_2$O)]$_n$	*P*-1	8.641 (3) 95.21 (2)	15.737 (4) 108.03 (2)	16.372 (5) 96.25 (2)	2.785	2.935 (H$_2$O)	[107–109]
[Ba$_4$(pta)$_8$]	*P*-1	14.382 (7) 79.43 (2)	15.777 (8) 82.21 (2)	20.613 (10) 82.34 (2)	2.753	–	[107–109]
[Ba(pta)$_2$(tet)]	$C2/c$	23.07 (1) –	9.898 (3) 93.26 (2)	15.813 (6) –	2.71	2.89 (tet)	[110]
[Ba(tdfnd)$_2$(tet)]	$P1/c$	17.150 (2) –	10.735 (5) 97.56 (7)	22.836 (7) –	2.710	2.856 (tet)	[111–115]
[Ba(tdfnd)$_2$(tet)] (disordered)	*Pbca*	12.381 (6) –	23.062 (9) –	29.138 (9) –	2.688	2.846 (tet)	[116]
[Ba(hfac)$_2$(H$_2$O)]$_n$	$P2_1/c$	8.659 (4) –	8.752 (4) 100.46 (4)	22.527 (9) –	2.790	2.93 (tet)	[89]
[enH$_2$]$_{1.5}$[Ba(hfac)$_5$]EtOH	$C2/c$	22.379 (7) –	12.143 (3) 102.22 (2)	33.820 (8) –	2.791	–	[50,51]
[Ba(hfac)$_2$(Et$_2$O)]$_n$	$P2_1/c$	11.276 (2) –	22.368 (2) 100.01 (2)	15.531 (3) –	2.68–2.82	–	[117,118]
[Ba(hfac)$_2$(EtOH)]$_n$	$P2_1/c$	11.523 (3) –	19.281 (8) 103.68 (3)	8.596 (3) –	2.769	2.915 (EtOH)	[103]
[Ba(hfac)$_2$(18-C-6)]	$P4_12_12$	14.421 (2)	–	15.494 (2)	2.82	–	[119,120]
[Ba(hfac)$_2$(18-C-6)]	$P2_1$	10.087 –	14.181 108.82 (1)	11.879 –	2.739	2.919 (18-C-6)	[64–68,96]
[Ba(hfac)$_2$(N-18–C-6)]	$P2_1/c$	12.945 (4) –	14.406 (2) 95.16 (2)	25.103 (6) –	2.848	2.815 (N-18–C-6)	[121]
[Ba(hfac)$_2$(tet)]	*P*-1	9.506 (1) 84.10 (1)	10.969 (1) 88.10 (1)	15.085 (1) 65.31 (1)	2.703	2.857 (tet)	[69]

Table 8 (*Continued*)

Compound	Space group	a/Å, α/°	b/Å, β/°	c/Å, γ/°	Average M–O (β-diket)/Å	Average M–O (L)/Å	References
$[Ba(hfac)_2(tet)]$	*P*-1	9.648 (2) 94.15 (1)	11.155 (2) 90.73 (1)	15.465 (3) 114.46 (1)	2.705	2.837 (tet)	[70,71]
$[Ba(hfac)_2(N\text{-}tet)]$	*Pbca*	21.69 (8) –	17.81 (7) –	15.74 (2) –	2.716	2.847 (N-tet)	[121]
$[Ba(hfac)_2(pent)]$	*C*2/*c*	20.074 –	14.331 106.77	23.334 –	2.787	2.837 (pent)	[122]
$[Ba(hfac)_2(CH_3O\{CH_2CH_2O\}_6 - nC_4H_9)]$	*P*-1	12.830 (2) 119.55 (1)	19.076 (2) 90.24 (2)	19.133 (3) 107.24	2.770	2.842 (glyme)	[123]
$[Ba(dmhd)_2(tet)]$ (disordered)	*C*2/*c*	48.821 –	7.866 109.76	17.923 –	2.664	2.961 (tet)	[124]
$[Ba(dppd)_2(tet)]$	*P*2$_1$/*a*	12.379 –	27.505 112.79	13.187 –	2.681	2.864 (tet)	[124]
$[Ba(diki)_2]$	*C*2/*c*	32.764 (6) –	12.110 (2) 102.12 (3)	15.690 (5) –	2.558	2.828 (N) 2.862 (O)	[125,126]
$[Ba(triki)_2]$	*Pccn*	24.939 (4) –	10.546 (2) –	14.349 (4) –	2.580	2.857 (N) 2.82 (O)	[125,126]
$[Ba(dpmiki)_2]_2$	*C*2/*c*	27.687 (5) –	10.453 (2) 101.88 (2)	22.679 (6) –	2.612	2.799 (O)	[125,126]
$[Ba_6(tmhd)_{12}(H_2O)_{13}]$	*R*3*c*	36.853 (11)	–	36.575 (15)	2.708	3.01 (H_2O)	[127]
$[Ba_5(tmhd)_5(Htmhd)_4(O)(OH)_3]$	*I*2/*a*	24.365 (9) –	21.174 (10) 100.98 (3)	48.486 (16) –	2.677	2.94 (O) 2.949 (OH)	[44–47]
$[Ba_6(tmhd)_{10}(O_2)(H_2O)_6]$	*Pbca*	18.546 (3) –	27.275 (6) –	29.872 (7) –	2.785	2.715 (H_2O) 2.90 (H_2O)	[128]
$[Ba_6(tmhd)_{10}(O_2)(H_2O)_6]$	*P*-1	15.834 (4) 80.09 (2)	16.190 (4) 64.95 (2)	16.423 (5) 67.83 (1)	2.735	2.72 (H_2O) 3.00 (H_2O)	[129]
$[Ba_6(tmhd)_{10}(O_2)(OH)_2(H_2O)_4]_2^- 2[HNEt_3]^+$	*P*-1	15.190 (2) 86.09 (2)	16.358 (2) 115.64 (3)	17.362 (3) 83.57	2.716	2.725 (H_2O) 2.79 (OH)	[130]
$[Ba_6(tmhd)_{10}(Me_2SiO)_2]$	*P*-1	14.731 (4) 73.98 (2)	18.605 (4) 83.31 (2)	28.507 (4) 75.72 (2)	–	3.180 (Me_2SiO)	[131]
$[Ba_6(tmhd)_4(piv)_8(py)_4]_2(py)$	*C*2/*c*	33.95 (2) –	18.214 (8) 115.01 (2)	27.123 (12) –	2.62	2.791 (piv) 2.968 (py)	[132]

Table 8 (*Continued*)

Compound	Space group	a/Å, α/°	b/Å, β/°	c/Å, γ/°	Average M–O (β-diket)/Å	Average M–O (L)/Å	References
$[Ba_7(tmhd)_2(piv)_{12}(py)_4(H_2O)_4]_2(py)$	$P2_1/n$	17.331 (3) –	18.194 (1) 91.03 (1)	22.871 (3) –	2.66	2.821 (piv) 3.03 (py) 2.745 (H_2O)	[61]
$[Ba_5(tmhd)_9Cl(H_2O)_7]$	P-1	17.082 (4) 71.36 (2)	17.152 (3) 75.02 (2)	26.274 (6) 76.16 (2)	2.712	3.203 (C1) 2.959 (H_2O)	[132]
$[Ba_5(tmhd)_9(piv)]$	$C2/c$	62.300 (14) –	14.929 (4) 116.45 (2)	32.500 (10) –	2.803	2.858 (piv)	[50,51]
$\{[Ba(tmhd)_2(MeOH)_3]MeOH\}_2$	P-1	10.693 (3) 109.26 (1)	10.720 (3) 91.9 (1)	15.627 (3) 94.86 (1)	2.670	2.795 (MeOH)	[58–60]
$[Ba(tmhd)_2(MeOH)_2(H_2O)_2]_n$	$C2/c$	27.801 (4) –	10.569 (1)	11.132 (9)	2.743	2.777 (MeOH) 2.720 (H_2O)	[133]
$[Ba_4(tmhd)_8]$ (hexane, 150 K)	P-1	14.969 (3) 62.47 (2)	13.836 (3) 65.98 (1)	14.822 (3) 60.78 (1)	2.765	–	[44–47]
$[Ba_4(tmhd)_8]$ (pentane)	P-1	14.903 (3) 65.92 (1)	15.084 (2) 60.36 (1)	15.190 (2) 61.84 (1)	2.749	–	[44–47]
$[Ba_4(tmhd)_8]$ (sublimed)	$Pbca$	26.244 (4) –	21.784 (4) –	18.128 (6) –	2.727	–	[58–60]
$[Ba(tmhd)_2(tet)]$ (150 K)	P-1	10.596 (5) 115.38 (1)	14.420 (2) 97.82 (1)	15.455 (2) 105.13 (2)	2.678	2.901 (tet)	[73]
$[Ba(tmhd)_2(tet)]$	P-1	10.606 (3) 115.31 (1)	14.452 (3) 97.74 (2)	15.463 (4) 105.15 (1)	2.683	2.893 (tet)	[70,71]
$[Ba(tmhd)_2(tri)]$	$P2_1/c$	10.686 (3) –	23.614 (6) 109.11 (2)	15.650 (3) –	2.628	2.865 (tri)	[88]
$[Ba(tmhd)_2(di)]_2$	P-1	10.431 (6) –	10.441 (6) 76.52 (3)	15.955 (7) –	2.615	2.859 (di)	[74,75]
$[Ba(tmhd)_2(di)(H_2O)_{0.5}]_2$	$C2/c$	29.857 (5) –	10.506 (3) 96.21 (2)	21.941 (7) –	2.66	2.87 (di) 3.05 (H_2O)	[134]
$[Ba(tmhd)_2(tmeda)_2]$	$C2/c$	14.970 (2) –	16.078 (2) 96.21 (2)	18.267 (2) –	2.67	3.04 (tmeda)	[135]
$[Ba(tmhd)_2(pmdeta)]$	$P2_1/c$	10.577 (3) –	23.547 (7) 105.21 (2)	15.963 (5) –	2.624	2.973 (pmdeta)	[136,137]

Table 8 (*Continued*)

Compound	Space group	a/Å, α/°	b/Å, β/°	c/Å, γ/°	Average M–O (β-diket)/Å	Average M–O (L)/Å	References
$[Ba(tmhd)_2(hmteta)]$	$P2_1/c$	10.833 (6) –	20.442 (12) 104.35 (4)	19.404 (9) –	2.649	2.986 (hmteta)	[136,137]
$[Ba(tmhd)_2(bipy)_2]_2$	$P\text{-}1$	12.067 (2) 92.40 (2)	14.807 (4) 105.56 (2)	21.459 (5) 104.31 (2)	2.769	2.91 (bipy)	[61]
$[Ba(tmhd)_2(NH_3)_2]_2$	$P\text{-}1$	10.450 (3) 93.58 (2)	10.567 (2) 110.54 (3)	13.794 (4) 91.17 (2)	2.741	2.905 (NH_3)	[62]
$[Ba(tmhd)_2(Et_2O)_2]_2$	$P2_1/n$	14.865 (2) –	14.533 (2) 110.54 (3)	14.789 (2) –	2.713	2.827 (Et_2O)	[57]
$[Ba_2(tmhd)_3(OCH_2CH_2OPr^i)$-$(HOCH_2CH_2OPr^i)]_2$	$C2/c$	30.899 (7) –	11.395 (2) 103.08 (1)	29.782 (5) –	2.729	2.867 (O)	[89]
$[Ba_5(OH)(tmhd)_5(OCHMe$-$CH_2NMe_2)_4]$	$P\text{-}1$	14.59 (2) 105.6 (1)	15.41 (2) 96.1 (1)	27.03 (3) 111.7 (1)	2.684	2.815 (OH) 2.96 (N)	[138]
$[Ba(tmhd)_2(HOCHMeCH_2NMe_2)]_2$	$P2_1/n$	10.767 (2) –	19.101 (4) 93.59 (2)	15.956 (3) –	2.777	2.962 (N)	[138]
$[Ba(tmhd)_2(HOAr)_2(thf)]_2$	$P\text{-}1$	13.190 (2) 112.43 (2)	16.081 (4) 97.28 (2)	16.152 (4) 109.06 (2)	2.723	2.909 (HOAr) 2.888 (thf)	[139]

[a] –Line indicates data that was not reported in the literature, or is otherwise not relevant to the compound described.

Table 9
Physical data for barium β-diketonate compounds[a]

Compound	Melting point (°C)	Sublimation temperature (°C)	Solubility, e, ar, alk	Thermal data (°C)	Other	References
[Ba(acac)$_2$(EtOH)]$_n$	Dec 210	–	sls, ns, ns	Four step dec	Ms	[103]
[Ba(acac)$_2$(18-C-6)(H$_2$O)$_{0.5}$]$_n$	Dec 135	–	s, s, s	Loss of L, then dec	NMR	[64–68]
[Ba(tclac)$_2$(H$_2$O)$_{0.5}$]$_n$	Dec 110–112	–	s, s, s	–	NMR	[64–68]
[Ba(tclac)$_2$(18-C-6)]$_n$	Dec 158–160	–	s, s, s	–	NMR	[64–68]
[Ba(dmhd)$_2$(tet)] (disordered)	–	–	–	–	NMR	[124]
[Ba(dppd)$_2$(EtOH)]$_n$	Dec 250	–	sls, ns, ns	Four step dec	Ms	[103]
[Ba(dppd)$_2$(tet)]	–	–	s, s, sls	Multi step dec	Ms	[124]
[Ba(dmpbd)$_2$]$_n$	Dec	–	–	–	–	[49]
[Ba(dnppd)$_2$(18-C-6)]$_n$	> 200	–	–	–	–	[64–68]
[Ba(tfac)$_2$]$_n$	170–235	205–215	s, s, s	–	Ms, dep	[95]
[Ba(tfac)$_2$(H$_2$O)$_{0.5}$]$_n$	Dec 168–230	–	s, s, s	Light sensitive	NMR	[64–68]
[Ba(tfac)$_2$(18-C-6)]$_n$	Dec 190–192	150–160 Partial	s, s, s	Loss of L, then subl	NMR	[64–68]
[Ba(tfac)$_2$(tet)]	133–136	150	s, s, s	Subl intact	Dep/vp	[70,71]
[Ba(tfac)$_2$(hmteta)]	143–147	–	s, s, sls	Loss of L, then subl	Ms	[106]
[Ba(dfhd)$_2$]$_n$	229	220	–	–	Ms	[140]
Ba(dfhd)$_2$(H$_2$O)]$_n$	200	–	s, s, sls	Loss of L, then dec	Dep	[141–143]
[Ba(ofhd)$_2$]$_n$	233	220	–	–	Ms	[140]
[Ba(pfdmhd)$_2$]$_n$	293	–	–	–	–	[141–143]
[Ba(pta)$_2$(H$_2$O)]$_n$	–	–	–	Loss of L, then subl	–	[107–109]
[Ba$_4$(pta)$_8$]		180–200	–	Subl intact	–	[107–109]
[Ba(pta)$_2$(tet)]	–	Partial subl 150 above that [Ba$_4$(pta)$_8$] 220–240	–	Partial dissoc	–	[110]
[Ba(tdfnd)$_2$(H$_2$O)]$_n$	187	Loss L, then subl	s, s, sls	Two step subl	Dep	[141–143]
[Ba(tdfnd)$_2$]$_n$	186	–	s, s, s	Subl intact two step	Dep	[141–143]
[Ba(tdfnd)$_2$(tet)]	70	90	s, s, s	Subl intact	Dep	[111–115]

Table 9 (*Continued*)

Compound	Melting point (°C)	Sublimation temperature (°C)	Solubility, e, ar, alk	Thermal data (°C)	Other	References
$[Ba(tdfnd)_2(tet)]$ (disordered)	61–63	90	s, s, s	Subl intact	Dep	[116]
$[Ba(hfac)_2]_n$	>210	205–215	s, s, s	–	Ms, dep	[95]
$[Ba(hfac)_2(H_2O)]_n$	–	–	–	–	NMR	[97]
$[enH_2]_{1.5}[Ba(hfac)_5]EtOH$	–	–	–	Two step subl	NMR	[44–47]
$[Ba(hfac)_2(Et_2O)]_n$	–	–	–	–	–	[117,118]
$[Ba(hfac)_2(EtOH)]_n$	Des 120	160–180	s, sls, ns	Three step dec	Ms	[103]
$[Ba(hfac)_4]$.2(pmdetaH)	53–56	–	s, s, s	–	Ms	[87]
$[Ba(hfac)_2$(18-C-6)]	185–188	165	s, s, s		NMR	[64–68,96,144,145]
$[Ba(hfac)_2$(N-18–C-6)]	236–240	135–137	–	–	Air stable	[121]
$[Ba(hfac)_2$(2N-18–C-6)$]_n$	–	–	–	–	–	[96]
$[Ba(hfac)_2(tet)]$	121–125	120	s, s, s	Subl intact	Dep/vp	[64–68,70,71,144, 145]
$[Ba(hfac)_2$(N-tet)]	167–169	129–136	–	Subl intact	Air stable	[121]
$[Ba(hfac)_2(pent)]$	146–147	123	–	Subl intact	Air stable	[122]
$[Ba(hfac)_2(hexa)]_n$	59–62	145	s, s, s	Subl intact	MW, air stable	[64–68]
$[Ba(hfac)_2(hept)_{0.5}]_n$	109–112	–	s, s, s	Subl intact	Air stable	[94]
$[Ba(hfac)_2(CH_3O\{CH_2CH_2O\}_6-nC_4H_9)]$	52–54	120	s, s, s	20% Residue	Dep, ms	[123]
$[Ba(hfac)_2(CH_3O\{CH_2CH_2O\}_5\text{-}C_2H_5)]_n$	109–110	100	s, s, s	–	Ms	[123]
$[Ba(dmmod)_2]_n$	Liquid	–	–	–	MW, ms	[146]
$[Ba(miki)_2]_n$	138–140	–	s, s, sls	39% Residue	MW, ms	[125,126]
$[Ba(diki)_2]$	170–171	–	s, s, sls	39% Residue	MW, ms	[125,126]
$[Ba(triki)_2]$	80–82	–	s, s, sls	29% Residue	MW, ms	[125,126]
$[Ba(dpmiki)_2]_2$	165–168	–	s, s, sls	26% Residue	MW, ms	[125,126]
$[Ba(dpdiki)_2]_n$	137–138	–	s, s, sls	33% Residue	MW, ms	[125,126]
$[Ba(dptriki)_2]_n$	127–128	–	s, s, sls	23% Residue	MW, ms	[125,126]
$[Ba_6(tmhd)_{12}(H_2O)_{13}]$	–	–	–	–	–	[127]
$[Ba_5(tmhd)_5(Htmhd)_4(O)\text{-}(OH)_3]$	–	–	–	–	Ms	[50,51]
$[Ba_6(tmhd)_{10}(O_2)(H_2O)_6]$	–	–	–	–	–	[128,129]

Table 9 (*Continued*)

Compound	Melting point (°C)	Sublimation temperature (°C)	Solubility, e, ar, alk	Thermal data (°C)	Other	References
$[Ba_6(tmhd)_{10}(O_2)(OH)_2(H_2O)_4]_2$-$2[HNEt_3]^+$	–	–	–	–	–	[130]
$[Ba_6(tmhd)_{10}(Me_2SiO)_2]$	–	–	–	–	–	[131]
$[Ba_6(tmhd)_4(piv)_8(py)_4].2(py)$	–	–	–	–	–	[132]
$[Ba_7(tmhd)_2(piv)_{12}(py)_4(H_2O)_4]._2(py)$	–	–	–	–	–	[61]
$Ba_5(tmhd)_9Cl(H_2O)_7]$	Des 90	–	–	Dec 310	–	[132]
$[Ba_5(tmhd)_9(piv)]$	–	–	–	–	–	[44–47]
$\{[Ba(tmhd)_2(MeOH)_3].MeOH\}_2$	–	–	–	Loss of L, then subl	Ms	[64–68]
$[Ba(tmhd)_2(MeOH)_2(H_2O)_2]_n$	–	–	–	Multi step dec	Ms	[133]
$[Ba_4(tmhd)_8]$ (hexane, 150 K)	194–197	190–210	s, s, s	Sublimes intact	Ms, low T NMR	[44–47]
$[Ba_4(tmhd)_8]$ (pentane)	–	190–230	–	–	–	[44–47]
$[Ba_4(tmhd)_8]$ (sublimed)	–	190–230	–	–	Vp	[64–68]
$[Ba(tmhd)_2(di)]_2$	93–95	–	s, s, s	Loss of L, then subl	Ms	[74,75]
$[Ba(tmhd)_2(tri)]$	77–79	–	s, s, s	Loss of L, then subl	Ms	[88]
$[Ba(tmhd)_2(tet)]$	90–92	–	s, s, s	Loss of L, then subl	Ms, dep	[70,71,147]
$[Ba(tmhd)_2(tmeda)_2]$	95–105	–	s, s, s	Loss of L, then subl	Ms	[135]
$[Ba(tmhd)_2(pmdeta)]$	–	–	s, s, s	Loss of L, then subl	Dep	[136,137]
$[Ba(tmhd)_2(hmteta)]$	–	–	s, s, s	Loss of L, then subl	Dep	[136,137]
$[Ba(tmhd)_2(bipy)_2]_2$	157	–	s, s, s	Loss of L, then subl	UV/vis	[61]
$[Ba(tmhd)_2(NH_3)_2]_2$	170–173	–	s, s, s	Loss of L, then subl	MW	[62]
$[Ba(tmhd)_2(Et_2O)_2]_2$	–	–	–	–	–	[57]

Table 9 (*Continued*)

Compound	Melting point (°C)	Sublimation temperature (°C)	Solubility, e, ar, alk	Thermal data (°C)	Other	References
$[Ba(tmhd)_2(o\text{-}phen)]_n$	216	–	s, s, s	Loss of L, then subl	MW	[63]
$[Ba(tmhd)_2(di)(H_2O)_{0.5}]_2$	–	–	–	–	–	[134]
$[Ba(tmhd)_2(18\text{-}C\text{-}6)(H_2O)_{0.5}]_n$	130–135	–	s, s, s	Loss of L, then subl	NMR	[64–68]
$[Ba_2(tmhd)_3(OCH_2CH_2OPr^i)\text{-}(HOCH_2CH_2OPr^i)]_2$	108–111	–	s, s, s	Four step dec	Ms	[93]
$[Ba(tmhd)_{1.5}(OEt)_{0.5}\text{-}(EtOH)_{0.33}]_n$	211–214	–	s, sls, ns	Three step dec	Ms	[93]
$[H_{0.5}Ba(tmhd)_{1.5}\text{-}(OCH_2CH_2OMe)]_n$	106–110	–	sls, sls, sls	Three step dec	Ms	[89]
$[Ba(tmhd)(bdmap)(EtOH)_{0.5}]_n$	Des 64	–	s, s, s	Four step dec	Ms	[103]
$[H_{0.33}Ba(tmhd)_{1.33}\text{-}(OCH_2CH_2N(Me)CH_2\text{-}CH_2NMe_2)]_n$	96–98	–	s, s, s	Four step dec	Ms	[103]
$[H_{0.5}Ba(tmhd)_{1.5}(O(CH_2\text{-}CH_2O)_2Me)]_n$	97–100	–	s, s, s	Five step dec	Ms	[103]
$[Ba(tmhd)(O\text{-}(CH_2CH_2O)_3Me)]_n$	69–72	–	s, s, s	Four step dec	Ms	[103]
$[Ba(tmhd)(O(CH_2CH_2O)_4\text{-}OH)]_n$	49–51	–	s, s, s	Four step dec	Ms	[103]
$[Ba(tmhd)_2(HO\text{-}(CH_2CH_2O)_2Me)]$	125–130	–	s, s, s	Loss of L, then subl	–	[136,137]
$[Ba(tmhd)_2(HO\text{-}(CH_2CH_2O)_3Me)]$	116–120	–	s, s, s	Loss of L, then subl	–	[136,137]
$[Ba_5(OH)(tmhd)_5(OCHMe\text{-}CH_2NMe_2)_4]$	–	–	s, s, s	Multi step dec	Ms	[138]
$[Ba(tmhd)_2(HOCHMe\text{-}CH_2NMe_2)]_2$	168	–	s, s, sls	Loss of L, then subl	Ms	[138]
$[Ba(tmhd)_2(HOAr)_2(thf)]_2$	–	–	s, s, s	Dec	Ms	[139]

[a] –Line indicates data that was not reported in the literature, or is otherwise not relevant to the compound described; dec, decomposes; des, desolvates; e, ethers (such as thf, Et_2O); ar, aromatic solvents such as toluene or benzene; and alk, alkanes (hydrocarbons) such as n-hexane or n-heptane; sublimatio temperatures are at 10^{-2} Torr or lower (reduced pressure); thermal data is at 1 atm.; subl, sublimes; L, adduct ligand; ms, mass spectrum reported; dep deposition reported with compound data; vp, vapor pressure reported; where a$_n$ is shown in the compound formula, it is denoting that the exact solid state formulation is not known (i.e. whether the compound is a monomer, dimer etc).

decrease the oligomerization of these materials has been heavily utilized by many research groups.

For ease of discussion, the compounds may be divided into five categories, large heteroleptic (penta-, hexa- and hepta-meric) clusters (1); infinite chains (2); homoleptic tetramers (3); dimers (4); and monomers (5). Taking each of these categories in turn.

11.1. Large heteroleptic clusters

Compounds with a central structural core of Ba_5, Ba_6, and Ba_7 have been reported. All incorporate the $tmhd^-$ β-diketonate ligand and have various anionic supporting ligands (e.g. Cl^-, O_2^{2-}, OH^-, Me_2SiO^-, and piv^-). Illustrative examples of (a) a Ba_5 core would be $[Ba_5(tmhd)_9Cl(H_2O)_7]$ (Fig. 23), [132] and $[Ba_5(O)(tmhd)_5(Htmhd)_4(OH)_3]$ (Fig. 4 above) [50,51]; (b) for Ba_6 core, the compound $[Ba_6(tmhd)_{10}(O_2)(H_2O)_6]$ (Fig. 24) [128]; and (c) for Ba_7, the compound $[Ba_7(tmhd)_2(piv)_{12}(py)_4(H_2O)_4]\cdot 2(py)$ [132].

11.2. Infinite chains

Barium compounds containing fluorinated β-diketonate ligands as well as water or other small molecules (e.g. Et_2O, EtOH) exhibit an infinite chain motif in the solid state [93,103,107–109,130]. This is readily illustrated in the compound $[Ba(hfac)_2(EtOH)]_\infty$ (Fig. 25) [103] where each barium center is ten coordinate, with two Ba–F bonds per metal center.

This perhaps explains why this type of compound often gives rise to BaF_2 when subjected to high temperatures [16–24,103]. Other compounds of this type include $[Ba(hfac)_2(Et_2O)]_\infty$, [117,118] $[Ba(hfac)_2(H_2O)]_\infty$, [97,98] and $[Ba(pta)_2(H_2O)]_\infty$ [107–109].

Another compound that consists of infinite chains, albeit held together via H-bonding, is $[Ba(tmhd)_2(MeOH)_2(H_2O)_2]_\infty$, [133] which has been referred to elsewhere as a monomer [133]. However, if the crystal packing of the molecule is examined, it readily can be seen that there are H-bonded chains through the MeOH and H_2O ligands (Fig. 26).

11.3. Homoleptic tetramers

If, as noted above, rigorous anaerobic techniques are observed, and all potential Lewis base adducts removed from the metal center's influence (e.g. in vacuo), then the true homoleptic barium tmhd and pta compounds may be isolated [44–47,107–109]. They have the general formula $[Ba_4(\beta\text{-diket})_8]$. The fluorinated compound $[Ba_4(pta)_8]$ (Fig. 27) has nine coordinate barium metal centers; two of the coordination positions on each metal are taken up by F atoms of the CF_3 groups on the β-diketonate ligand. When the β-diket is tmhd, two distinct structural motifs of $[Ba_4(tmhd)_8]$ have been observed (orthorhombic {not shown} and triclinic {Fig. 28}) [44–47,58–60].

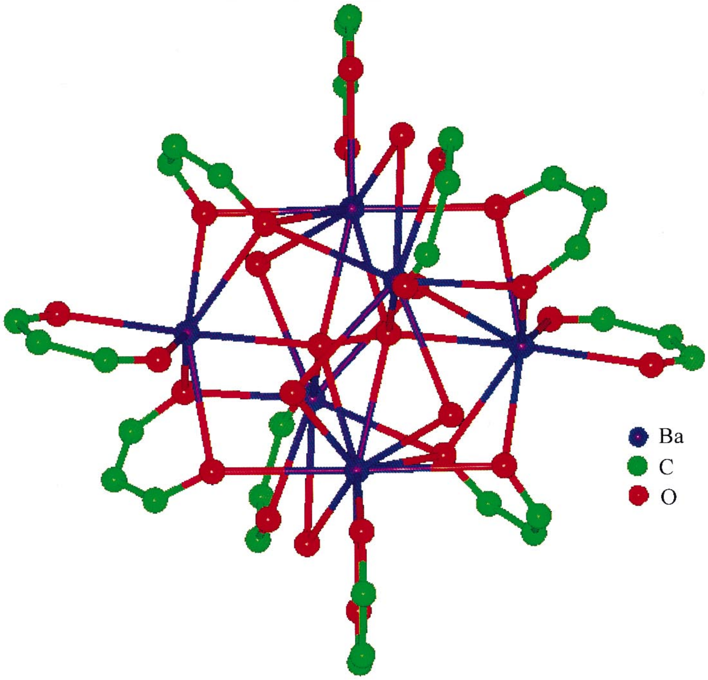


Fig. 24

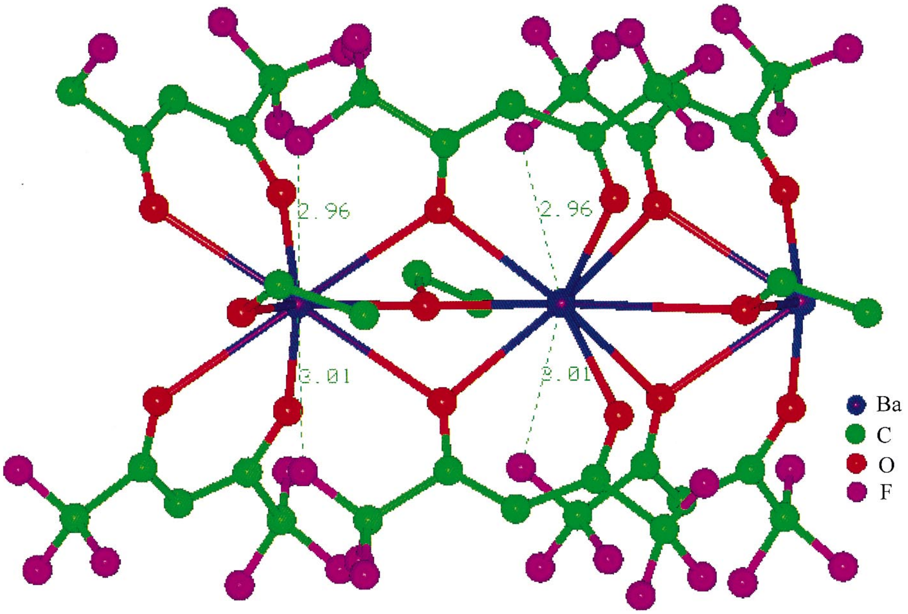


Fig. 25

Fig. 24. Molecular structure of [$Ba_6(tmhd)_{10}(O_2)(H_2O)_6$] [128].
Fig. 25. Molecular structure of [$Ba(hfac)_2(EtOH)]_\infty$ [103].

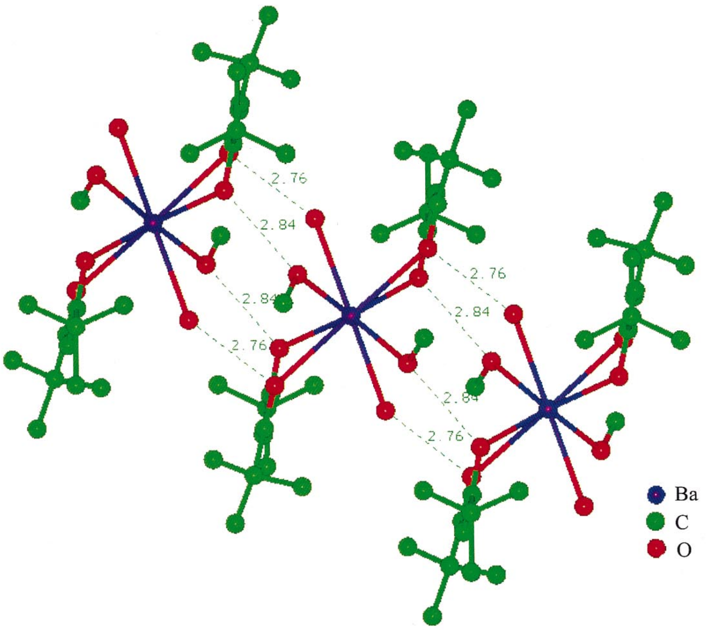


Fig. 26

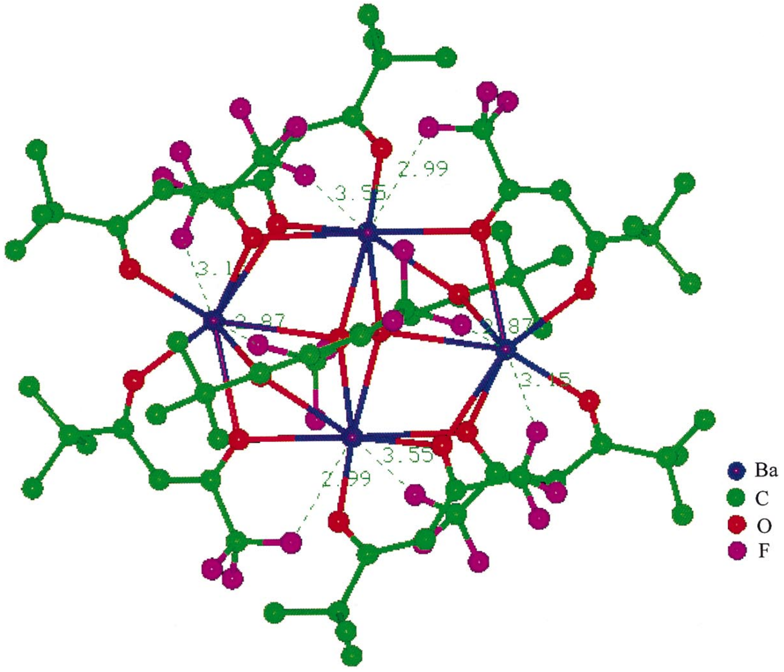


Fig. 27

Fig. 26. Molecular structure of $[Ba(tmhd)_2(MeOH)_2(H_2O)_2]_\infty$ [133].
Fig. 27. Molecular structure of $[Ba_4(pta)_8]$ [107–109].

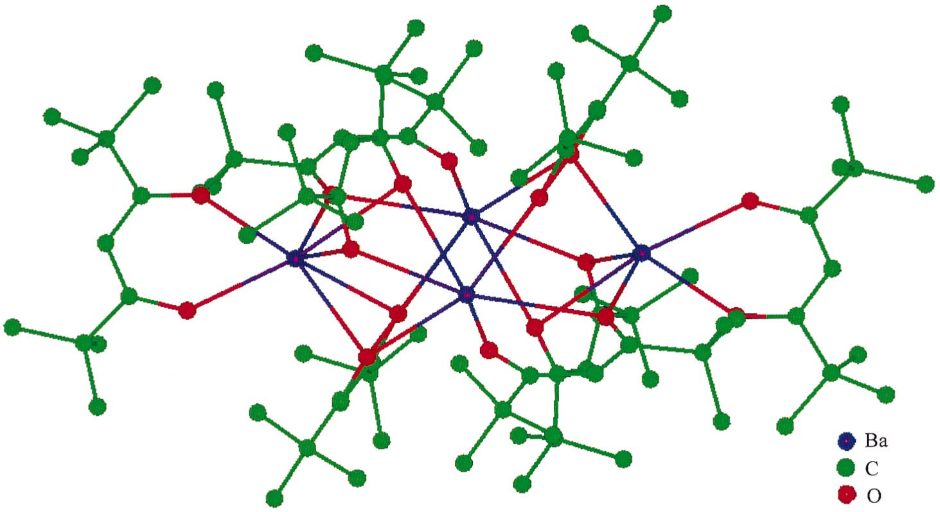


Fig. 28

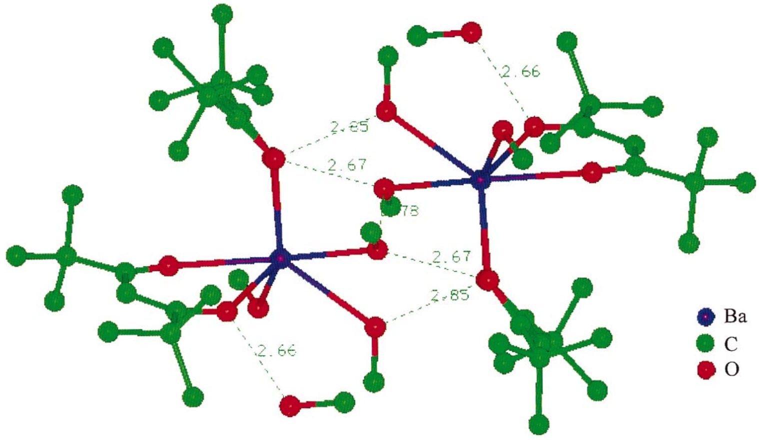


Fig. 29

Fig. 28. Molecular structure of $[Ba_4(tmhd)_8]$ [44–47].
Fig. 29. Molecular structure of $\{[Ba(tmhd)_2(MeOH)_3]MeOH\}_2$ [58–60].

$[Ba_4(tmhd)_8]$ is heavily utilized in the thin films industry for the deposition of BaO (usually as part of $YBa_2Cu_3O_{7-x}$), [16–24] and is very sensitive to water and air. Thus, it is commonly stored in vacuo or under inert gas (Ar or N_2). It should ideally be colorless, but is often observed to exhibit a pale yellow color (indicating some denaturing of the compound).

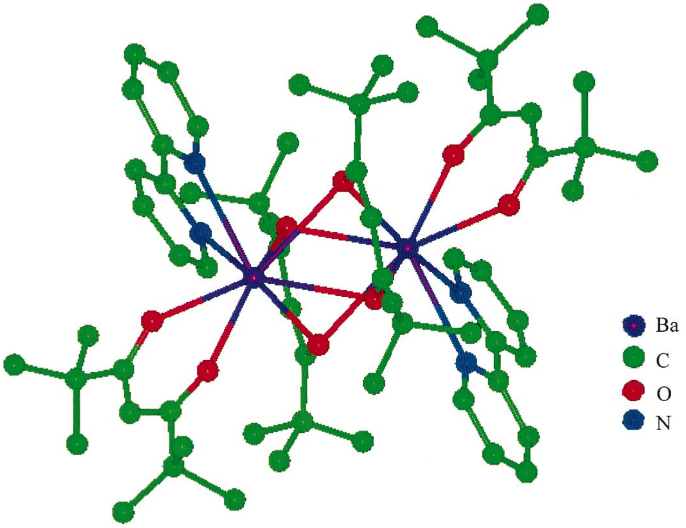


Fig. 30

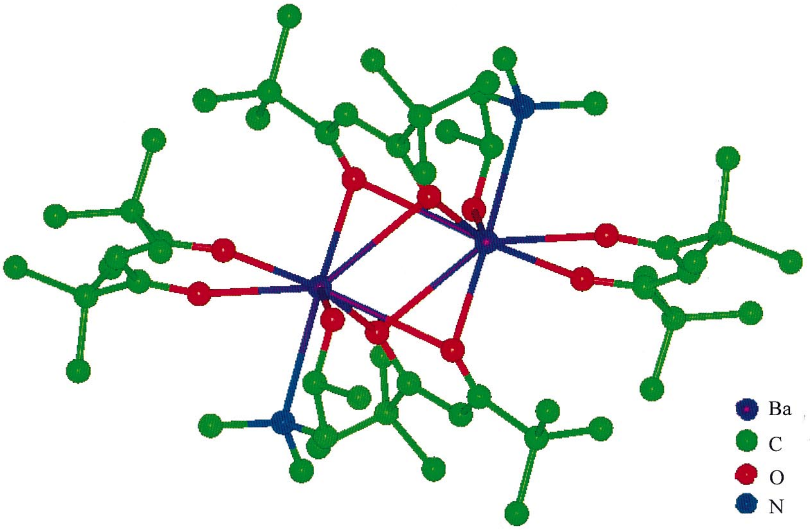
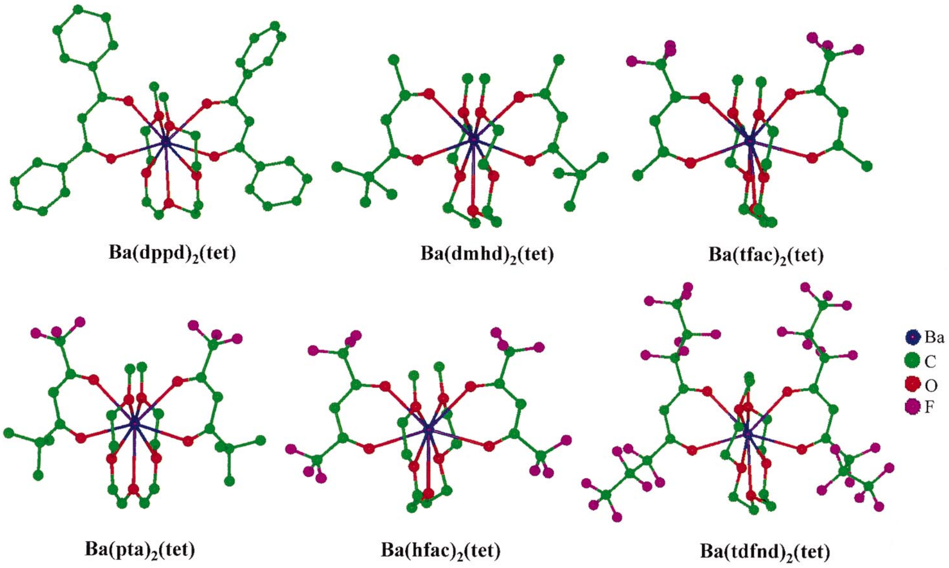


Fig. 31

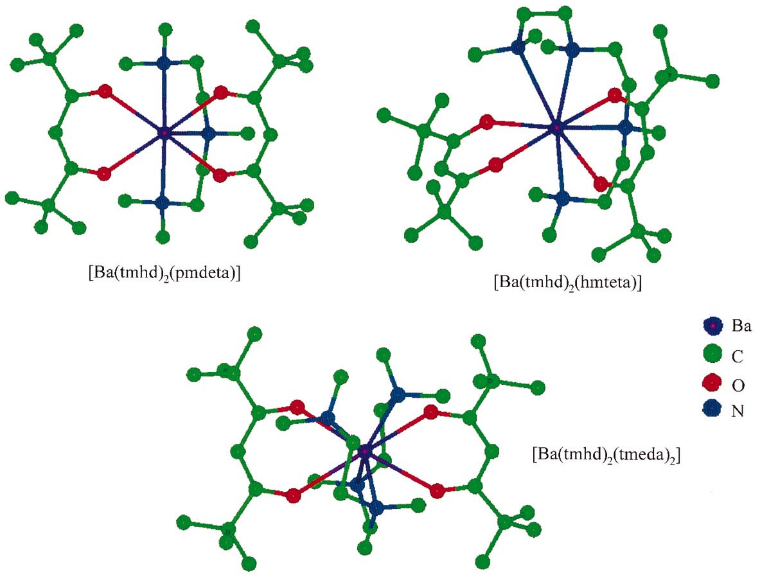
Fig. 30. Molecular structure of $[Ba(tmhd)_2(bipy)_2]_2$ [61].
Fig. 31. Molecular structure of $[Ba(tmhd)_2(HOCHMeCH_2NMe_2)]_2$ [138].



$Ba(dppd)_2(tet)$ **$Ba(dmhd)_2(tet)$** **$Ba(tfac)_2(tet)$**

$Ba(pta)_2(tet)$ **$Ba(hfac)_2(tet)$** **$Ba(tdfnd)_2(tet)$**

Fig. 32



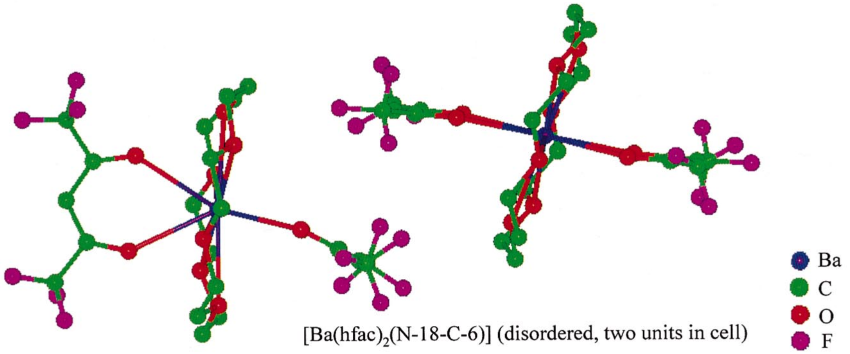
$[Ba(tmhd)_2(pmdeta)]$ $[Ba(tmhd)_2(hmteta)]$

$[Ba(tmhd)_2(tmeda)_2]$

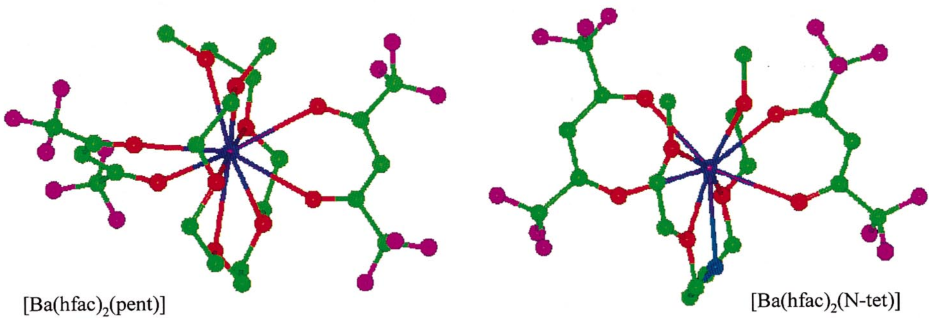
Fig. 33

Fig. 32. Molecular structures of some $[Ba(\beta\text{-diket})_2(tet)]$ compounds (where β-diket, dmhd; dppd; pta; tfac; hfac; and tdfnd) [64–68,70,71,111–115,124].

Fig. 33. Molecular structures of some $[Ba(tmhd)_2(amine)]$ compounds (where amine, hmteta; pmdeta; and tmeda) [135–137].



$[Ba(hfac)_2(N\text{-}18\text{-}C\text{-}6)]$ (disordered, two units in cell)



$[Ba(hfac)_2(pent)]$

$[Ba(hfac)_2(N\text{-}tet)]$

Fig. 34

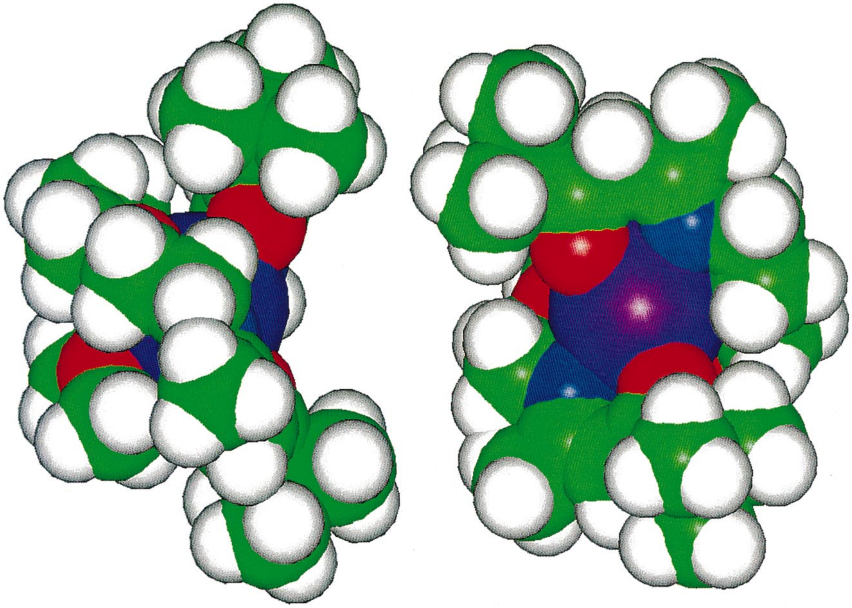


Fig. 35

Fig. 34. Molecular structures of some $[Ba(hfac)_2(adduct)]$ compounds (where adduct, N-18–C-6; pent; and N-tet) [121,122].

Fig. 35. Molecular structure of $[Ba(diki)_2]$ [125,126].

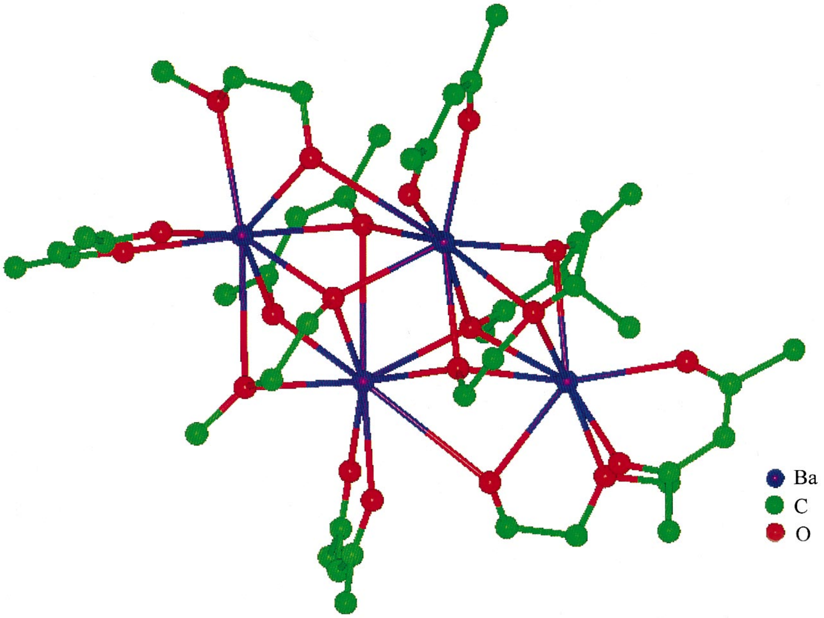


Fig. 36

Fig. 36. Molecular structure of $[Ba_2(tmhd)_3(OCH_2CH_2OPr^i)(HOCH_2CH_2OPr^i)]_2$ [89].

11.4. Dimers

The formation of dimeric species is common for barium β-diketonate compounds especially when the β-diketonate ligand is tmhd, and small adduct molecules are available to fulfill the metal centers coordination requirements. This has been alluded to above (Fig. 5).

Further examples of this structural class are, $\{[Ba(tmhd)_2(MeOH)_3]MeOH\}_2$ (Fig. 29), [58–60] a H-bonded dimer; $[Ba(tmhd)_2(NH_3)_2]_2$ (Fig. 5), [62] $[Ba(tmhd)_2(bipy)_2]_2$ (Fig. 30), [61] $[Ba(tmhd)_2(HOCHMeCH_2NMe_2)]_2$ (Fig. 31), [138] $[Ba(tmhd)_2(HOAr)_2(thf)_2]_2$ [139] and $[Ba(tmhd)_2(di)]_2$ [74,75]. All of the dimeric compounds are thermally unstable, losing their adducts prior to sublimation of the parent $[Ba(tmhd)_2]_x$ compound [44–47,74,75].

11.5. Monomers

Monomeric barium β-diketonate compounds comprise by far the largest category. They all have one feature in common; a multidentate Lewis base is utilized to saturate the coordination sphere around the barium metal center (e.g. crown ethers such as 18-C-6 [64–68,103], N-18–C-6 [87]; hexa- [64–68], penta- [122], tetra- [76,78], azatetra- [121] and tri-glyme [88]; and also amines such as hmteta, [107–109,136,137] pmdeta [136,137], and tmeda [135]). The degree of binding of these Lewis bases varies with regard to the β-diketonate ligand attached to the metal center [124]. Thus, hfac and tdfnd compounds with glyme ligands are volatile and sublime intact, [70,71,122,123] whereas tmhd compounds tend to dissociate prior to sublimation (a more detailed study of this phenomenon may be found in [124]). Illustrated below are some of these compounds (Figs. 32–34).

Another class of compounds to be mentioned was synthesized by Marks et al. [125,126] and these incorporate β-diketoiminate ligands (where one of the oxygens of a β-diketonate has been replaced by a nitrogen with a pendant side arm to further coordinate to the metal center). An example of this type of compound, [Ba(diki)$_2$] can be seen in Fig. 35. Unfortunately, these compounds are reported to be pyrophoric and to decompose on heating [125,126].

As for calcium and strontium, there have also been studies on a number of barium mixed alkoxide/β-diketonate ligand compounds [89,103]. An illustrative example is the compound $[Ba_2(tmhd)_3(OCH_2CH_2OPr^i)(HOCH_2CH_2OPr^i)]_2$ (Fig. 36) [89]. As with calcium, these compounds are not volatile.

Studies on the use of 'scorpion tail' type β-diketonate ligands (e.g. dmmod$^-$), whilst of potential interest, (due to the liquid nature of the compounds formed with barium), have yet to yield promising CVD precursors, as the compounds decompose below their vapor phase transport temperatures [146,148].

Acknowledgements

In an effort to be as representative as practicable of the state-of-the-art in the present subject matter, Professor P. O'Brien is gratefully acknowledged for graciously permitting the utilization in this review of previously unpublished results from his laboratories that he has shared with us. We would also like to thank Dr A.A. Drozdov, Dr P. Miele, Dr J. Vaissermann, Professor L. Hubert-Pfalzgraf, Professor A.H. Rheingold, and Professor A. Gleizes for providing atomic coordinates of certain molecules. This enabled the depiction, by the Biosym™ package Insight II, of the molecular structures contained within this review.

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