

Synthesis and Structures of Volatile Mononuclear and Pentanuclear Chelates of Barium

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Received September 2, 1992*

The structures of two Ba(II) chelates of β -diketonates have been determined; one is mononuclear and the other is multinuclear. The Ba(II) chelate of the anion of 2,2,6,6-tetramethyl-3,5-heptanedione (thd) recrystallized from pentane formed monoclinic crystals, space group $I2/a$, with dimensions $a = 24.365(9)$ Å, $b = 21.174(10)$ Å, $c = 48.486(16)$ Å, $\beta = 100.98(3)^\circ$, and $Z = 8$. This structure was determined to be a β -diketonate deficient pentanuclear complex with the formula $Ba_5(thd)_9(H_2O)_3(OH)$. Both β -diketonate and water ligands act as bridges between barium ions in this structure, resulting in a thermally unstable compound. A new mononuclear anionic Ba(II) chelate of 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (hfa) has been synthesized. X-ray diffraction analysis of the monoclinic (space group $C2/c$) crystals gave a unit cell of dimensions $a = 22.379(7)$ Å, $b = 12.143(3)$ Å, $c = 34.800(8)$ Å, $\beta = 102.22(2)^\circ$, and $Z = 8$; its structure was determined to be $(ethylenediamine-H_2)_1.5[Ba(hfa)_5] \cdot C_2H_5OH$. The thermal properties of $(enH_2)_{1.5}[Ba(hfa)_5] \cdot C_2H_5OH$ were investigated by thermogravimetric analysis. It was determined that this mononuclear anionic complex is volatile and thermally stable when compared to previously reported Ba(II) β -diketonate complexes.

Introduction

In our studies of β -diketonate metal chelates used as precursors in metal organic chemical vapor deposition (MOCVD) of thin film superconductors,^{1,2} we have investigated the crystal structure of a pentanuclear Ba(II) complex of the anion of 2,2,6,6-tetramethyl-3,5-heptanedione (thd). In addition, a new volatile mononuclear barium chelate of the anion of 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (hfa) has been synthesized and its crystal structure has been determined.

MOCVD is one of the most effective methods for making superconducting thin films. Several groups have made high quality superconducting thin films using this method.²⁻⁸ However, a major problem with this method is that barium cannot readily be transported to the substrate stoichiometrically because barium precursors, compared with the copper(II) and yttrium(III) precursors, have relatively low volatility and thermal stability.

Many crystal structures of the first- and second-group metal β -diketonate chelates have been reported, and these have been reviewed by Fenton.⁹ The crystal structures of these complexes are interesting because the chelates tend to exist as oligomers. For example, Hollander et al. have studied the structures of the strontium(II) and calcium(II) complexes of the anion of 1,3-diphenyl-1,3-propanedione, solvated with ethanol or acetone, and found that they are tetrameric, with some of the β -diketonate

ligands coordinated in a bidentate manner to a single metal ion and other ligands serving as bridges between two metal ions.^{10,11} Sahbari and Olmstead¹² have described the structure of sodium acetylacetonate hydrate as oligomeric. The structure of potassium acetylacetonate hemihydrate also has a water bonded to the metal ion.¹³

Several complexes of Ba(II) and oxygenated ligands have been studied,¹⁴⁻¹⁹ and the coordination number of the barium ions in these structures ranges from 7 to 12. Although several of these structures are monomeric barium complexes made with macrocyclic ligands,¹⁵⁻¹⁷ Yokomori has studied a series of substituted malonate complexes of Ba(II) and has found that these structures are polymeric.¹⁹ In these structures, both water and malonate anions serve as bridges between barium ions to form an extensive polymer with metal ion binding to all donor atoms in the anion.

One approach to limit the oligomerization in these complexes, and thereby increase their volatility, is to coordinate the metal ions with neutral ligands. Van der Sluis et al., for example, have used the polyether tetraglyme to obtain a monomeric complex with the formula $Ba(hfa)_2(\text{tetraglyme})$.²⁰ A report of the structure of a Ba(II) complex of thd recrystallized from methanol shows that solvent molecules can act as neutral ligands to give what appears to be a mononuclear complex,²¹ but this does not survive

* Abstract published in *Advance ACS Abstracts*, January 1, 1994.

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Table 1. Crystal and Intensity Measurement Data for $\text{Ba}_5(\text{thd})_9(\text{H}_2\text{O})_3(\text{OH})$ and $(\text{enH}_2)_{1.5}[\text{Ba}(\text{hfa})_5] \cdot \text{C}_2\text{H}_5\text{OH}$

chem formula	$\text{Ba}_5\text{C}_{99}\text{H}_{178}\text{O}_{22}$	$\text{BaC}_{30}\text{H}_{26}\text{O}_{11}\text{N}_3\text{F}_{30}$
fw	2407.1	1311.8
dimens, mm	$0.2 \times 0.45 \times 0.6$	$0.04 \times 0.33 \times 0.4$
<i>a</i> , Å	24.365(9) ^a	22.379(7)
<i>b</i> , Å	21.174(10)	12.143(3)
<i>c</i> , Å	48.486(16)	34.800(8)
β , deg	100.98(3)	102.22(2)
<i>V</i> , Å ³	24 556(17)	9242(4)
<i>Z</i>	8	8
<i>D</i> (calcd), g/cm ³	1.302	1.878
<i>D</i> (obsd), g/cm ³	1.30	ND
<i>F</i> (000), e	9824.0	5088.0
μ (Mo <i>K</i> α), cm ⁻¹	16.34	16.34
temp, °C	25	-110
space group	<i>I2/a</i>	<i>C2/c</i>
<i>R</i> ^b	0.0550	0.0591
<i>R</i> _w ^b	0.0691	0.0588

^a Estimated standard deviations in the least significant figure(s) are given in parentheses. ^b The quantity minimized in the least-squares procedures is $\sum w(|F_o| - |F_c|)^2$. $R = R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $R_w = R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w(F_o)^2]^{1/2}$.

sublimation, and the structure of the sublimate has not been established. In another example of this approach, Rees et al. have reported a new dimeric complex prepared by reacting ammonia with the thd chelate of Ba(II) to give a compound with the structure $[\text{Ba}(\text{thd})_2 \cdot 2\text{NH}_3]_2$.²²

Formation of an anionic chelate is another approach to making metal ions more highly coordinated so that formation of oligomers is prevented. Several structures of anionic β -diketonate chelates have been reported. For example, Bennett et al. described the structure of $\text{Cs}[\text{Y}(\text{hfa})_4]$, in which yttrium is octacoordinate with four β -diketonate groups.²³ Fenton et al. have studied $\text{Rb}_2[\text{Na}(\text{hfa})_3]$, in which sodium is six-coordinate.²⁴ The structure of $(\text{TMNDH})[\text{Mg}(\text{hfa})_3]$ (in which TMNDH is monoprotonated 1,8-bis(dimethylamino)naphthalene) has also been determined. The results of this study show that magnesium is octahedrally coordinated by the anions and the proton lies between the two nitrogens in the plane of the naphthalene ring. There is no obvious interaction between the cation and the anion.²⁵

In the present study, we have determined the crystal structure of the Ba(II) chelate of the anion of 2,2,6,6-tetramethyl-3,5-heptanedione recrystallized from pentane. The results from this work show it to be the oligomeric, β -diketonate deficient species $\text{Ba}_5(\text{thd})_9(\text{H}_2\text{O})_3(\text{OH})$. We are also reporting the structure of a new highly volatile barium chelate, $(\text{enH}_2)_{1.5}[\text{Ba}(\text{hfa})_5]$, in which enH_2 is diprotonated ethylenediamine. The barium ion is coordinated by nine oxygen atoms of the β -diketonates, while the protonated en molecules in the lattice are weakly hydrogen-bonded to the chelate anions. This is one of the first monomeric β -diketonate barium chelates known which is produced by forming an anionic chelate.

Experimental Section

Structure Determination of the Ba(II) Complex of thd. Single crystals suitable for X-ray diffraction studies were obtained by dissolving the oligomeric thd complex, freshly made from $\text{Ba}(\text{OH})_2$,^{1,26} in warm *n*-pentane, filtering the solution, covering the beaker with Parafilm, and allowing the solvent to evaporate very slowly. Crystal structure information is summarized in Table 1. The density of the crystals, measured experimentally by flotation methods using toluene and chloroform, is in good agreement with the calculated value. Data were collected using a

Nicolet P3/F diffractometer with Mo *K*α radiation ($\lambda = 0.71073$ Å). The unit cell was determined to be monoclinic (space group *I2/a*) with dimensions $a = 24.365(9)$ Å, $b = 21.174(10)$ Å, $c = 48.486(16)$ Å, and $\beta = 100.98(3)^\circ$. Semiempirical absorption corrections were made. The crystal structure was solved using the direct-methods option in the SHELXTL-PLUS program. Because of the large number of parameters, the final model was refined using blocked full-matrix least-squares procedures. The barium and oxygens were included in all cycles of refinement. The carbons of the thd ligands were divided into 3 blocks. All atoms except the 18 disordered methyl carbons were refined anisotropically. Hydrogen atoms attached to ordered carbons were included in idealized positions. Water hydrogens (7 or 8) and hydrogen atoms attached to disordered carbons (54) were not included in the final model. Tables of atomic coordinates, equivalent isotropic displacement parameters, and anisotropic displacement parameters are included in the supplementary material. The final residuals were $R = 0.0550$ and $R_w = 0.0691$.

Synthesis and Structure Determination of the Ba(II) Complex Containing hfa, enH₂, and CH₃CH₂OH. Synthesis of $(\text{enH}_2)_{1.5}[\text{Ba}(\text{hfa})_5] \cdot \text{C}_2\text{H}_5\text{OH}$. $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ (0.5 mmol, 157 mg, Fisher) and H(hfa) (2 mmol, 0.28 mL, Aldrich) were mixed with stirring in 50 mL of ethanol. After the barium hydroxide was dissolved, 5 mL of an ethanolic solution of ethylenediamine (0.5 mmol, 30 mg, Fisher) was added. The reaction mixture was stirred at room temperature for 30 min and filtered to remove a very small amount of unreacted barium residue. The ethanol was removed by an aspirator, leaving a highly concentrated solution. Fine crystals formed after a small amount of CH_2Cl_2 was added to this solution, and the headspace above the mixture was evacuated very gently with an aspirator. This product was collected by filtration and dried in a desiccator. The isolation of the corresponding anionic Ba(II) chelate of 2,2,6,6-tetramethyl-3,5-heptanedione, H(thd), was unsuccessful.

Elemental Analysis. Barium was determined gravimetrically by the standard BaSO_4 precipitation technique. Carbon, hydrogen, and nitrogen were determined by combustion analysis, and the data were provided by Huffman Analytical Laboratory (Golden, CO). Anal. Calcd for $\text{BaC}_{30}\text{H}_{26}\text{O}_{11}\text{N}_3\text{F}_{30}$: Ba, 10.5; C, 27.5; H, 2.00; N, 3.20. Found: Ba, 10.1; C, 27.0; H, 1.89; N, 3.41. It should be mentioned that, as shown by the crystal structure determination, the same product was obtained when the ratio of starting materials Ba:en:H(hfa) was changed from 1:1:4 to 1:1.5:5.

¹H NMR. The proton NMR spectrum of $(\text{enH}_2)_{1.5}[\text{Ba}(\text{hfa})_5] \cdot \text{C}_2\text{H}_5\text{OH}$ dissolved in D_2O was obtained at room temperature on a FT-NMR, VXR-300s spectrometer. The $-\text{CH}-$ (hfa) resonance appeared at 5.76 ppm (relative to tetramethylsilane), and the $-\text{CH}_2-$ (enH_2) resonance was at 3.19 ppm in the expected ratio of 5:6. Low-intensity resonances due to ethanol were also observed.

Structure Determination. Single-crystal X-ray analysis of this chelate was performed on two different samples at two different temperatures. In one experiment, the data were collected at room temperature with a crystal of the product synthesized in a Ba:en:H(hfa) ratio of 1:1:4. The unit cell was determined to be monoclinic (space group *C2/c*) with dimensions $a = 22.655(5)$ Å, $b = 12.437(2)$ Å, $c = 34.930(7)$ Å, and $\beta = 102.53(3)^\circ$. Of 6959 reflections measured, 6253 were unique and 2581 were observed ($F > 4\sigma(F)$). Because of the disorder in the fluorine atoms and the low ratio of observations to parameters, 6.5:1, with only the barium, oxygens, and nitrogens treated anisotropically, refinement was terminated with $R = 0.093$. The solution based on this data set gave the structure corresponding to the formulation $(\text{enH}_2)_{1.5}[\text{Ba}(\text{hfa})_5] \cdot \text{C}_2\text{H}_5\text{OH}$.

The result was much improved by collecting data at -110 °C, and all results reported here are based on this low-temperature data set. In this structure analysis, the unit cell was determined to be monoclinic (space group *C2/c*) with dimensions $a = 22.379$ Å, $b = 12.143$ Å, $c = 34.800$ Å, and $\beta = 102.22^\circ$. The shortened unit cell dimensions can be attributed to the lower temperature. The crystal for the low-temperature X-ray analysis was synthesized using a Ba:en:H(hfa) ratio of 1:1.5:5, and the analysis shows the structure to be the same as the structure determined in the room-temperature experiment. This structure was solved using Patterson and Fourier techniques. In the final model, one CF_3 group and the ethyl group of the associated (hydrogen-bound) ethanol were disordered. All other atoms were refined anisotropically. Hydrogen atoms were included in idealized positions after difference maps indicated some of their positions. The use of these idealized positions may confuse the evaluation of hydrogen-bonding patterns, but there are insufficient data to refine their positions. The final residuals were $R = 0.0591$ and $R_w = 0.0588$ for 4027 observed reflections ($F > 4\sigma(F)$) and 673 variables.

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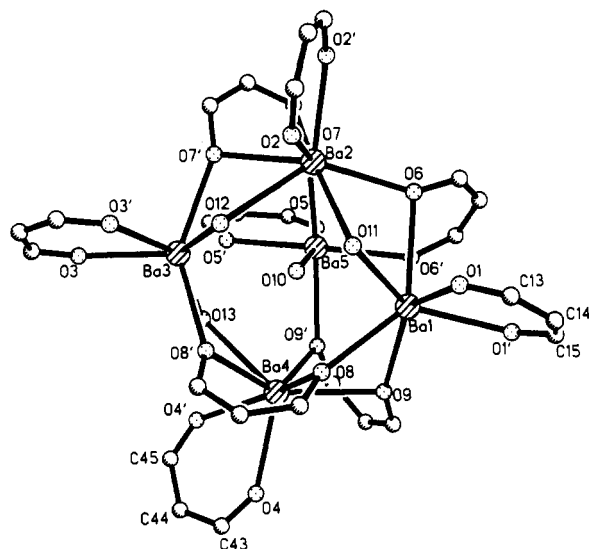


Figure 1. Structure of $\text{Ba}_5(\text{thd})_9(\text{H}_2\text{O})_3(\text{OH})$. The *tert*-butyl carbons, all hydrogen atoms, and parentheses in atom labels have been omitted for clarity. In two examples, the carbons on two ligands have been labeled C(13), C(14), and C(15) in the chelate with oxygens O(1) and O(1') and C(43), C(44), and C(45) in the ring with O(4) and O(4').

Tables of atomic coordinates and equivalent isotropic displacement parameters and anisotropic parameters are included in the supplementary material.

Results

The results from the structure determination of the barium complex of the anion of H(thd) that crystallized from *n*-pentane showed that the structure is oligomeric, with five barium ions arrayed in a cluster with approximately a square pyramidal geometry (Figure 1). These metal centers are connected by bridging oxygens of three kinds, those in carbonyl, water, and hydroxide moieties. Only nine β -diketonate ligands are present, whereas ten were expected on the basis of the formation of a coordinately saturated, electrically neutral complex. Therefore, a hydroxy group is needed to preserve electroneutrality. Five of the β -diketonate ligands are bidentate ligands (1–5) and are bonded only to a single barium ion, and the carbonyl oxygens of the other four ligands (6–9) act as bridges between two barium ions. There are also three oxygens (O(11), O(12), O(13)) in aquo moieties which act as bridges between barium ions and one oxygen (O(10)) which appears to be a hydroxyl group bonded to the barium at the apex of the pyramid.

Selected bond distances for this structure are listed in Table 2. The carbonyls in the ligands that are bidentate to one barium ion have Ba–O distances in the range 2.57–2.71 Å. In general, the Ba–O distances of the carbonyls in the bridging β -diketonate ligands are slightly longer, ranging from 2.61 to 2.82 Å. Discrimination between aquo groups and hydroxyl groups is difficult, but assignments were made by using relative Ba–O bond lengths. The bond lengths of three of the four nonchelated oxygens (O(11), O(12), O(13)) are in the range 2.78–3.07 Å, with O(13)–Ba(3) as the shortest of these bonds (2.78 Å). These are attributed to the aquo ligands. The oxygen labeled O(10) makes contacts of 2.92–3.16 Å with the barium ions which make up the base of the pyramidal structure. However, it is only 2.66 Å from the barium at the apex of the pyramid, Ba(5). Therefore, the oxygen which is located inside the Ba ion cluster is assigned as a hydroxyl group. These conclusions are consistent with the observation that metal–oxygen bond distances are shorter by approximately 0.35 Å when the anion of a solvent, rather than the protonated solvent, is bonded.²⁷ The short distances between O(10) and

Table 2. Barium–Oxygen Bond Distances (Å) in $\text{Ba}_5(\text{thd})_9(\text{H}_2\text{O})_3(\text{OH})$

O(1)–Ba(1)	2.717(9) ^a	O(1')–Ba(1)	2.601(10)
O(2)–Ba(2)	2.670(10)	O(2')–Ba(2)	2.590(11)
O(3)–Ba(3)	2.569(9)	O(3')–Ba(3)	2.634(9)
O(4)–Ba(4)	2.570(10)	O(4')–Ba(4)	2.638(11)
O(5)–Ba(5)	2.602(9)	O(5')–Ba(5)	2.622(9)
O(6)–Ba(1)	2.789(9)	O(6)–Ba(2)	2.678(9)
O(6')–Ba(1)	2.778(8)	O(6')–Ba(5)	2.639(9)
O(7)–Ba(2)	2.778(9)	O(7)–Ba(5)	2.664(11)
O(7')–Ba(2)	2.761(10)	O(7')–Ba(3)	2.610(10)
O(8)–Ba(1)	2.822(9)	O(8)–Ba(4)	2.727(9)
O(8')–Ba(3)	2.666(10)	O(8')–Ba(4)	2.710(9)
O(9)–Ba(1)	2.761(11)	O(9)–Ba(4)	2.764(10)
O(9')–Ba(4)	2.713(9)	O(9')–Ba(5)	2.631(11)
O(10)–Ba(1)	2.980(9)	O(10)–Ba(2)	2.924(9)
O(10)–Ba(3)	2.984(8)	O(10)–Ba(4)	3.155(9)
O(10)–Ba(5)	2.661(8)		
O(11)–Ba(1)	3.069(10)	O(11)–Ba(2)	2.872(9)
O(12)–Ba(2)	3.037(10)	O(12)–Ba(3)	2.941(10)
O(13)–Ba(3)	2.780(9)	O(13)–Ba(4)	2.997(9)

^a Estimated standard deviations in the least significant figure(s) are given in parentheses.

Table 3. Selected Bond Angles (deg) in $\text{Ba}_5(\text{thd})_9(\text{H}_2\text{O})_3(\text{OH})$

O(1)–C(13)–C(14)	123.9(12) ^a	C(54)–C(55)–O(5')	122.4(17)
C(13)–C(14)–C(15)	130.6(16)	O(6)–C(63)–C(64)	119.8(11)
C(14)–C(15)–O(1')	122.5(15)	C(63)–C(64)–C(65)	129.0(14)
O(2)–C(23)–C(24)	124.8(12)	C(64)–C(65)–O(6')	123.7(16)
C(23)–C(24)–C(25)	126.8(17)	O(7)–C(73)–C(74)	119.9(12)
C(24)–C(25)–O(2')	126.6(14)	C(73)–C(74)–C(75)	129.2(15)
O(3)–C(33)–C(34)	123.8(15)	C(74)–C(75)–O(7')	122.4(14)
C(33)–C(34)–C(35)	127.6(15)	O(8)–C(83)–C(84)	122.6(13)
C(34)–C(35)–O(3')	126.1(14)	C(83)–C(84)–C(85)	129.6(13)
O(4)–C(43)–C(44)	123.3(13)	C(84)–C(85)–O(8')	125.4(13)
C(43)–C(44)–C(45)	126.1(18)	O(9)–C(93)–C(94)	120.3(18)
C(44)–C(45)–O(4')	125.3(14)	C(93)–C(94)–C(95)	130.7(19)
O(5')–C(55)–C(54)	126.4(12)	C(94)–C(95)–O(9')	122.5(15)
C(53)–C(54)–C(55)	126.1(16)		

^a Estimated standard deviations in the least significant figure(s) are given in parentheses.

Table 4. Selected Bond Distances (Å) in $\text{Ba}_5(\text{thd})_9(\text{H}_2\text{O})_3(\text{OH})$

O(1)–C(13)	1.296(18) ^a	O(1')–C(15)	1.290(18)
C(13)–C(14)	1.380(24)	C(14)–C(15)	1.338(28)
O(2)–C(23)	1.278(18)	O(2')–C(25)	1.308(20)
C(23)–C(24)	1.345(28)	C(24)–C(25)	1.365(22)
O(3)–C(33)	1.276(19)	O(3')–C(35)	1.279(18)
C(33)–C(34)	1.366(26)	C(34)–C(35)	1.357(22)
O(4)–C(43)	1.268(18)	O(4')–C(45)	1.237(19)
C(43)–C(44)	1.452(26)	C(44)–C(45)	1.406(27)
O(5)–C(53)	1.249(21)	O(5')–C(55)	1.307(19)
C(53)–C(54)	1.451(28)	C(54)–C(55)	1.418(23)
O(6)–C(63)	1.251(18)	C(6')–C(65)	1.292(18)
C(63)–C(64)	1.436(22)	C(64)–C(65)	1.384(23)
O(7)–C(73)	1.284(18)	O(7')–C(75)	1.270(21)
C(73)–C(74)	1.424(23)	C(74)–C(75)	1.395(22)
O(8)–C(83)	1.280(17)	O(8')–C(85)	1.246(17)
C(83)–C(84)	1.404(23)	C(84)–C(85)	1.378(22)
O(9)–C(93)	1.277(22)	O(9')–C(95)	1.274(2)
C(93)–C(94)	1.384(26)	C(94)–C(95)	1.457(27)

^a Estimated standard deviations in the least significant figure(s) are given in parentheses.

Ba(1), Ba(2), Ba(3), and Ba(4) may indicate some interaction of oxygen with these metal ions. However, a consideration of distances expected from Coulomb's law, with equal charges assumed for all barium ions, suggests that these interactions are 20–30% less for these contacts than among other Ba–O bonds.

Selected carbon–oxygen and carbon–carbon distances are shown in Table 3 and selected bond angles are shown in Table 4. As can be seen, the C–O bond distances and angles are not affected greatly by whether the chelate is acting as a bridge between barium ions or is bidentate and coordinated to only one metal ion. Several of the *tert*-butyl groups (C(12), C(22), C(46),

(27) Iwata, Y. Doctoral Thesis, University of New Mexico, Albuquerque, NM, 1986.

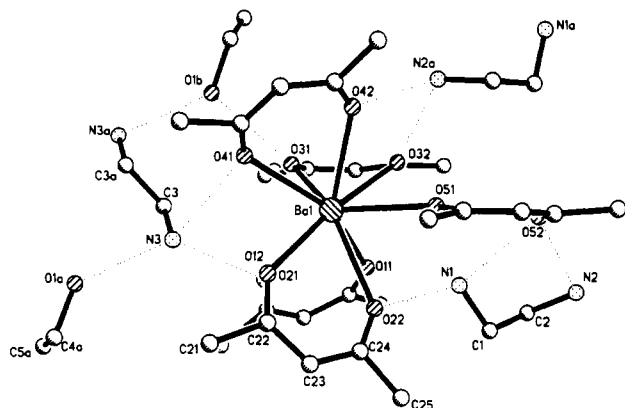


Figure 2. Diagram showing the coordination around the barium ion in $(\text{enH}_2)_{1.5}[\text{Ba}(\text{hfa})_5] \cdot \text{C}_2\text{H}_5\text{OH}$. Dotted lines indicate hydrogen-bonding between amine protons on ethylenediamine and oxygen atoms. In the figure the ethanols and N(3), C(3) and N(3a), C(3a) are related by the symmetry operator $-x, -y, -z$. The N(1), N(2) and N(1a), N(2a) amines are related by $1/2 - x, y - 1/2, 1/2 - z$. For clarity all hydrogens, fluorines, and parentheses in atom labels have been omitted. Representative labels on some of the carbon atoms are shown.

C(52), C(62), C(72) were disordered. These were modeled during the structure refinement by fixing the bond angles and distances for the *tert*-butyl carbons to those of idealized tetrahedral geometry. The occupancies and thermal parameters of these carbons were refined independently. The resulting model appears chemically reasonable. The final model, as shown in Figure 1, is consistent with the formulation $\text{Ba}_5(\text{thd})_9(\text{H}_2\text{O})_3(\text{OH})$. The result is consistent with the mass spectral and elemental analysis evidence published previously.¹

By contrast, the X-ray analysis of the Ba(II) chelate synthesized with H(hfa) and en is a monomeric structure with the formula $(\text{enH}_2)_{1.5}[\text{Ba}(\text{hfa})_5] \cdot \text{C}_2\text{H}_5\text{OH}$. There are eight molecules in each unit cell. The barium ion is coordinated with nine oxygen atoms from five surrounding β -diketonate hfa enolates, forming a complex anion, $[\text{Ba}(\text{hfa})_5]^{3-}$ (see Figure 2). There are one and one-half fully protonated en molecules situated between the complex anions to balance the charges. An uncoordinated ethanol is inserted in a hole between the cation and the anion. As described in the Experimental Section, the same product was obtained regardless of whether the ratio of starting materials was in a 1:1:4 or in a 1:1.5:5 ratio. This suggests that the coordination shown in this structure is the most stable for this β -diketonate anion chelate, at least in the solid state.

It is interesting that only nine oxygens in five ligands are coordinated to the barium, leaving one uncoordinated oxygen. Because barium macrocyclic chelates with coordination numbers as high as 11 are known,¹⁶ it is apparent that the barium ion in the present compound is not completely coordinated. The Ba–O bond distances, which are listed in Table 5, range from 2.729(6) to 2.860(7) Å. They are within the range expected on the basis of summed ionic radii of 2.74 Å for barium and oxygen and of values determined for other complexes.^{20,21} Other selected bond distances and angles are listed in Tables 5 and 6.

The one and one-half protonated en moieties are bound to the complex anion by forming hydrogen bonds with hfa in the same and in adjacent ions. Usually if a hydrogen bond forms between an amine and an oxygen, then the nitrogen–oxygen distance is expected to lie in the range 2.57–3.22 Å, with the N–H–O angle within 30° of linear.²⁸ Table 7 gives the distances between nitrogen and oxygen which are in this range. For example, there are four nitrogen–oxygen contacts around N(1) in the range 2.790–2.901 Å. However, only two of these contacts, N(1)–O(52) and N(1)–O(22), appear to be geometrically reasonable for hydrogen-

Table 5. Selected Bond Distances (Å) in $(\text{enH}_2)_{1.5}[\text{Ba}(\text{hfa})_5] \cdot \text{C}_2\text{H}_5\text{OH}$

Ba(1)–O(11)	2.860(7) ^a	Ba(1)–O(12)	2.811(7)
Ba(1)–O(21)	2.729(6)	Ba(1)–O(22)	2.768(6)
Ba(1)–O(31)	2.773(7)	Ba(1)–O(32)	2.771(6)
Ba(1)–O(41)	2.788(6)	Ba(1)–O(42)	2.825(6)
Ba(1)–O(51)	2.801(6)	Ba(1)–F(53)	3.285(8)
O(11)–C(12)	1.266(13)	O(12)–C(14)	1.243(14)
C(12)–C(13)	1.403(13)	C(13)–C(14)	1.398(15)
O(21)–C(22)	1.235(13)	O(22)–C(24)	1.242(12)
C(22)–C(23)	1.392(14)	C(23)–C(24)	1.383(13)
O(31)–C(32)	1.233(13)	O(32)–C(34)	1.247(15)
C(32)–C(33)	1.411(13)	C(33)–C(34)	1.410(16)
O(41)–C(42)	1.258(14)	O(42)–C(44)	1.249(12)
C(42)–C(43)	1.369(14)	C(43)–C(44)	1.401(12)
O(51)–C(52)	1.241(14)	O(52)–C(54)	1.258(15)
C(52)–C(53)	1.396(14)	C(53)–C(54)	1.379(16)

^a Estimated standard deviations in the least significant figure(s) are given in parentheses.

Table 6. Selected Bond Angles (deg) in $(\text{enH}_2)_{1.5}[\text{Ba}(\text{hfa})_5] \cdot \text{C}_2\text{H}_5\text{OH}$

O(11)–Ba(1)–O(12)	61.8(2) ^a	C(32)–C(33)–C(34)	122.9(11)
O(21)–Ba(1)–O(22)	63.9(2)	O(31)–C(32)–C(33)	127.3(10)
O(31)–Ba(1)–O(32)	62.7(2)	C(33)–C(34)–O(32)	128.6(9)
O(41)–Ba(1)–O(42)	62.5(2)	C(42)–C(43)–C(44)	123.3(10)
O(11)–C(12)–C(13)	127.1(10)	O(41)–C(42)–C(43)	130.4(9)
C(13)–C(14)–O(12)	130.7(9)	C(43)–C(44)–O(42)	128.0(9)
C(12)–C(13)–C(14)	122.6(10)	C(52)–C(53)–C(54)	123.4(11)
O(21)–C(22)–C(23)	128.5(9)	O(51)–C(52)–C(53)	126.0(10)
C(23)–C(24)–O(22)	129.1(9)	C(53)–C(54)–O(52)	128.0(10)
C(22)–C(23)–C(24)	123.8(9)		

^a Estimated standard deviations in the least significant figure(s) are given in parentheses.

Table 7. Hydrogen-Bond Lengths (Å) in $(\text{enH}_2)_{1.5}[\text{Ba}(\text{hfa})_5] \cdot \text{C}_2\text{H}_5\text{OH}$

N(1)–O(11)	2.790(11) ^a	N(2)–O(52)	2.823(11)
N(1)–O(22)	2.811(9)	N(3)–O(12)	2.844(10)
N(1)–O(51)	2.901(10)	N(3)–O(21)	3.008(10)
N(1)–O(52)	2.809(11)	N(3)–O(41)	3.003(10)
N(2)–O(32a)	2.733(11)	N(3)–O(1)	2.723(11)
N(2)–O(42a)	2.752(9)	O(1)–O(31a)	2.879(10)

^a Estimated standard deviations in the least significant figure(s) are given in parentheses.

bonding. From the data it appears that N(2) forms three hydrogen bonds to O(32a), O(42a), and O(52). Examination of the geometry of these oxygens around N(2) indicates that all three hydrogen bonds exist in this structure. The geometry around the atom N(3) suggests that it is hydrogen-bonded to O(12), O(41), and O(1a), the oxygen atom from the ethanol, but not to O(21). The ethanol oxygen, O(1a), also appears to have a hydrogen-bonding interaction with O(31a), as well as with N(3).

As expected, the ring carbon–carbon bond distances and the oxygen–carbon bond distances are virtually the same, e.g., C(12)–C(13) = 1.403 Å, C(13)–C(14) = 1.398 Å, O(11)–C(12) = 1.266 Å, and O(12)–C(14) = 1.243 Å. These data are consistent with the delocalization of the enol ring of H(hfa) in which the proton appears to be located in the ring plane, as determined by gas-phase electron diffraction.²⁹ However, the angles O–C–C = 126.0–130.7° and C–C–C = 122.6–123.8° in the chelate rings are greater than those in the enol ring of H(hfa), 126.4 and 115.2°, respectively. This suggests that the anionic chelate has a bite larger than that in the protonated form when it is coordinated to Ba(II). There are no significant distinguishing differences in bond lengths and bond angles among the five ligands. Even though in the solid state one ligand is coordinated to the barium ion through only one oxygen atom and the other four ligands are bidentate, in the NMR spectrum in D₂O solution only one peak

(28) Stout, G. H.; Jensen, L. H. *X-ray Structure Determination: A Practical Guide*; Macmillan: New York, 1968; p 303.

(29) Anderassen, A. L.; Zebelman, D.; Bauer, S. H. *J. Am. Chem. Soc.* **1971**, *93*, 1148.

for $-\text{CH}-$ (hfa) appears, presumably because the ligands are involved in rapid dynamic changes in solution, so that magnetic environments are averaged on the NMR time scale.

Discussion

There are several aspects of both structures that are unique. Although polymeric and oligomeric structures of oxygenated alkaline earth metal complexes have been determined previously, the square pyramidal geometry of the barium ions in the structure of $\text{Ba}_5(\text{thd})_9(\text{H}_2\text{O})_3(\text{OH})$ is unusual. It is also interesting to note that the most stable species that crystallizes from *n*-pentane is β -diketonate deficient, with a hydroxyl group substituted for the tenth thd ligand, which would be expected in a chelatively-saturated formulation. The Ca(II) and Sr(II) chelates of the anion of 1,3-diphenyl-1,3-propanedione (dpp) also form a cluster, tetrameric rather than pentameric, with some of the ligands acting as bridges between the metal ions.^{10,11} There is also a report of a square pyramidal barium complex.³⁰ These structures, however, do not show a β -diketonate ligand deficiency, and although these compounds are solvated, the solvent molecules (acetone or ethanol) are associated with only one calcium or strontium and do not serve as bridges between metal ions. The differences between the crystal structures of the Ca(II) and Sr(II) chelates of dpp and that of the Ba(II) chelate of thd are most likely due to differences in ligand geometry, metal ion size, and methods of synthesis (the dpp chelates were not synthesized from aqueous hydroxide solutions of the metal ions).

β -Diketonate ligands forming bridges between alkaline earth metal ions is also shown in the $[\text{Ba}(\text{thd})_2 \cdot 2\text{NH}_3]_2$ structure reported by Rees et al.²² In this case, each barium ion is coordinated by one bidentate ligand and two thd ligands bridge the two metal ions. Two neutral ammonia moieties are also bonded to each metal ion to give a coordination number of 8 for each barium ion. Another Ba(II) thd complex recrystallized from methanol demonstrates that methanol can act as a neutral ligand, which eliminates β -diketonate ligands bridging between metal ions. This resulted in a mononuclear complex with the formula $\text{Ba}(\text{thd})_2[\text{CH}_3\text{OH}]_3$, in which the barium ion was coordinated by seven oxygens.²¹

In some ways the presently determined pentanuclear structure is similar to the Ba(II) substituted malonate complexes described by Yokomori et al.,¹⁹ in that both water and oxygenated ligand serve as bridges between barium ions. The Ba(II) complex of thd, however, exists as discrete oligomers of five barium ions in a cluster, rather than as a polymeric chain. The coordination number of the barium ions in the thd structure that we have studied depends upon their positions in the structure, with the barium ion at the apex of the pyramid (Ba(5)) and one of the barium ions in the base of the structure (Ba(3)) having coordination numbers of 6, and the other metal ions having coordination numbers of 7. These represent rather low coordination numbers for barium. Consequently, it is not surprising to see the water molecules and hydroxyl group acting as auxiliary ligands in this structure. This causes this complex to be thermally unstable and undergo self-hydrolysis, as we have noted earlier.¹

The structure of the $(\text{enH}_2)_{1.5}[\text{Ba}(\text{hfa})_5] \cdot \text{C}_2\text{H}_5\text{OH}$ complex is also unique. The fact that it is a monomeric Ba(II) β -diketonate complex is in distinct contrast to the $\text{Ba}_5(\text{thd})_9(\text{H}_2\text{O})_3(\text{OH})$ structure and to those of most other alkaline earth metal β -diketonate complexes studied. In addition to that of the $\text{Ba}(\text{thd})_2 \cdot 3\text{CH}_3\text{OH}$ complex, another report of a monomeric Ba(II) β -diketonate complex is the recent example by Van der Sluis et al.,²⁰ which claims that the tetraglyme adduct $\text{Ba}(\text{hfa})_2$ -tetraglyme is monomeric. This group also uses H(hfa), but rather than forming an anionic chelate, they used a neutral donor ligand to retard oligomerization. This structure is also different from that

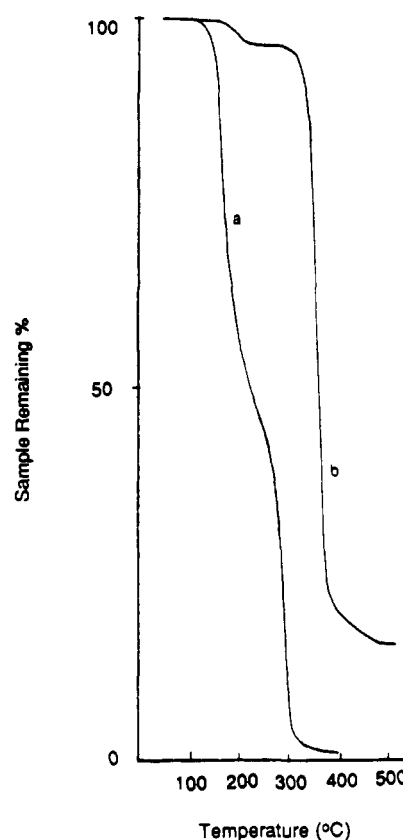


Figure 3. Thermogravimetric analysis of $(\text{enH}_2)_{1.5}[\text{Ba}(\text{hfa})_5] \cdot \text{C}_2\text{H}_5\text{OH}$ (a) and $[\text{Ba}(\text{hfa})_2]_n$ (b). Thermograms were obtained using a temperature program of $40^\circ\text{C}/\text{min}$ and a flow rate of 80 mL of helium/min.

of (TMNDH)[Mg(hfa)₃], another anionic chelate, in which the organic base simply acts as a counterion, in contrast with the hydrogen bonding between the en and hfa which occurs in our structure.

Further analysis of the two structures described here shows that, compared with the bonds between barium and carbonyls of $2.569\text{--}2.822\text{ \AA}$ in the β -diketonate cluster structure for $\text{Ba}_5(\text{thd})_9(\text{H}_2\text{O})_3(\text{OH})$, the Ba–O bond lengths in $(\text{enH}_2)_{1.5}[\text{Ba}(\text{hfa})_5] \cdot \text{C}_2\text{H}_5\text{OH}$ are more uniform. This is probably because the ligands in the monomeric structure are less distorted than those in an oligomeric structure. The O–C–C angles of the Ba(II) complex of hfa and en are larger, $127.3\text{--}130.7^\circ$, than those in the thd cluster, $119.8\text{--}126.6^\circ$, but the C–C–C angles are smaller, $122.6\text{--}123.8^\circ$, as compared with $126.1\text{--}130.7^\circ$ in the thd structure.

The most important practical property of the β -diketonate complexes is their volatility. In addition to providing an interesting comparison to other structures of oxygenated alkaline earth metal complexes studied previously, the results from the X-ray crystal determination of the Ba(II) complex of thd are important because this compound has been used extensively for the MOCVD of thin films of the high-temperature superconductor $\text{YBa}_2\text{Cu}_3\text{O}_7$.²⁻⁸ The structure analysis indicates that this compound can exist in the solid phase as oligomers, and this could account, at least in part, for its low volatility and poor thermal stability.¹ This suggests that the decomposition of this precursor to form a mixed-metal oxide on a substrate in MOCVD may be occurring primarily by hydrolysis, rather than by oxidation, as has commonly been assumed. It is also possible to limit the degree of hydrolysis and thermal decomposition that often occurs in the transport of precursors by conventional MOCVD. Sievers and Hansen³¹ recently demonstrated that $\text{Ba}_5(\text{thd})_9(\text{H}_2\text{O})_3(\text{OH})$ can be used as a precursor in a new process, termed supercritical fluid transport–chemical deposition, for forming coatings from ther-

(30) Caulton, K. G.; Chisholm, M. H.; Drake, S. R.; Huffman, J. C. *J. Chem. Soc., Chem. Commun.* 1990, 1498.

(31) Sievers, R. E.; Hansen, B. N. U. S. Patent No. 4,970,093, Nov 13, 1990.

mally labile precursors that decompose in MOCVD. In this process, metal chelates are first dissolved in a supercritical fluid such as carbon dioxide, nitrous oxide, or *n*-pentane (at elevated temperature and pressure) and the supercritical fluid solution is then pumped with a HPLC pump through a fused-silica capillary restrictor. As the metal chelates dissolved in the supercritical fluid emerge from the end of the capillary heated at ca. 200 °C, they vaporize and contact a substrate heated at about 500 °C to form films. In this process, thermal stability of the precursors is less important than it is in MOCVD.

On the other hand, the anionic chelate $(enH_2)_{1.5}[Ba(hfa)_5] \cdot C_2H_5OH$ is a better candidate for potential use as a precursor for traditional MOCVD, because of its higher thermal stability. Anionic chelates are known to be volatile.^{19,32} For example, Sievers et al. reported a β -diketonate anion chelate with high volatility, $(C_2H_5)_3NH[Eu(hfa)_4]$, and the following dissociation was proposed to occur during the evaporation:³²



It is expected that increasing the temperature would continuously drive the equilibrium toward the side favored by the removal of the more volatile products by the carrier gas. The TGA curve for $(enH_2)_{1.5}[Ba(hfa)_5] \cdot C_2H_5OH$ also reveals two steps (Figure 3), which suggests that the dissociation also occurs during vaporization for this compound. Figure 3 also shows the TGA curve of another barium chelate, $[Ba(hfa)_2]_n$, which is confirmed to be oligomeric by mass spectrometry.³³ The vaporization of

$[Ba(hfa)_2]_n$ occurs at about 340 °C with 15–19% sample remaining, while the vaporization of $(enH_2)_{1.5}[Ba(hfa)_5] \cdot C_2H_5OH$ occurs at a lower temperature (centering at about 280 °C) and yields less residue (1–4%). It is evident that, for the same ligand, the monomeric chelate $(enH_2)_{1.5}[Ba(hfa)_5] \cdot C_2H_5OH$ is more volatile than the oligomeric $[Ba(hfa)_2]_n$. The thermal analysis also shows this compound to be more volatile than the previously reported monomeric $Ba(thd)_2 \cdot 3CH_3OH$ compound, which has a vaporization temperature centered above 300 °C and has 10% sample remaining.²¹ On the basis of these thermogravimetric results, the mononuclear anionic complex $(enH_2)_{1.5}[Ba(hfa)_5] \cdot C_2H_5OH$ should be a superior precursor for use in the MOCVD of thin films containing barium.

Acknowledgment. Partial support for this work was provided by the Colorado Advanced Materials Institute. L.H. is grateful for support under the visiting fellows program of the Cooperative Institute for Research in Environmental Sciences at the University of Colorado.

Supplementary Material Available: Figures showing labeling of atoms on ligands and listings of crystal data, data collection conditions, and solution refinement details (Tables 1s and 7s), atomic coordinates and equivalent isotropic displacement parameters (Tables 2s and 8s), bond lengths (Tables 3s and 9s), bond angles (Tables 4s and 10s), anisotropic displacement parameters (5s and 11s), and hydrogen atom coordinates and isotropic displacement parameters (6s and 12s) (43 pages). Ordering information is given on any current masthead page.

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(33) Purdy, A. P.; Berry, A. D.; Holm, R. T.; Fatemi, M.; Gaskill, D. K. *Inorg. Chem.* **1989**, *28*, 2788.