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Articles

Anhydrous Yttrium Acetylacetonate and the Course of Thermal "Dehydration" of $Y(acac)_3{\cdot}3H_2O$

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Hydrocarbon-soluble $[Y(acac)_3]_n$ (acac = acetylacetonate) is produced in high yield by treatment of $Y[N(SiMe_3)_2]_3$ with 3 equiv of Hacac in hydrocarbon solvent. Variable-temperature ^1H and ^{89}Y NMR studies suggest that the degree of aggregation, n, of this compound is four. Attempted slow crystallization of this compound from hexanes gives, as the least-soluble material, the product of adventitious partial hydrolysis: $Y_4(OH)_2(acac)_{10}$. Its structure was established by X-ray diffraction as $Y_4(\mu_3\text{-}OH)_2(\mu\text{-}acac)_6(acac)_4$. This centrosymmetric aggregate has a diamond-shaped Y_4 core, with μ_3-OH groups lying above and below the Y_4 plane. The aggregation is further enforced by six acac ligands which have one oxygen terminal and the second bridging two yttrium atoms. Each of the remaining four acac ligands are fully terminal on a different yttrium such that every metal achieves coordination number eight. Various methods to produce this compound in high yield are discussed, including controlled vacuum thermolysis of bulk solid $Y(acac)_3{\cdot}3H_2O$, which gives, after recrystallization from benzene, $Y_4(OH)_2(acac)_{10}{\cdot}4C_6H_6$. This solid contains the same molecules isolated earlier, packed together in the lattice with benzene molecules. The loss of Hacac on vacuum thermolysis is suggested to be initiated by the hydrogen bonding to acac oxygen which exists in solid $Y(acac)_3{\cdot}3H_2O$. Crystal data for $Y_4(OH)_2(acac)_{10}$ (at −174 °C): a = 14.621(4) Å, b = 15.365(4) Å, c = 14.786(5) Å, and β = 116.13(2)° with Z = 2 in space group $P2_1/n$. For $Y_4(OH)_2(acac)_{10}{\cdot}4C_6H_6$ (at −175 °C): a = 13.606(4) Å, b = 13.951(5) Å, c = 11.366(4) Å, α = 96.70(2)°, β = 112.39(1)°, and γ = 78.57(2)° with Z = 2 in space group $P\bar{1}$.

Introduction

The Lewis base-free acetylacetonate compounds of the larger trivalent metals, $M(acac)_3$, show a tendency towards aggregation in order to achieve a coordination number higher than six.[1-3] Nevertheless, in the case of yttrium, whose $[Y(acac)_3]_n$ is not fully characterized,[4a] it is surprising that there are reports that its volatility[4b] is too low to allow it to serve as a precursor for chemical vapor deposition (CVD). *If* it is a monomer (n = 1), higher volatility would be expected. Most such work begins with the readily-accessible (from aqueous solution) and structurally-characterized[5] trihydrate, $Y(acac)_3{\cdot}3H_2O$, which is presumed to undergo thermal "dehydration" under CVD conditions. We report here our attempts to use modern synthetic methods to directly produce $[Y(acac)_3]_n$, as well as a study of the true course of attempts to dehydrate the trihydrate.

Experimental Section

All procedures involved in the synthesis and characterization of $Y(acac)_3$ were carried out under an atmosphere of nitrogen or in vacuo. All organic solvents were dried and distilled prior to use. NMR spectra (^1H) were recorded on both a Nicolet 360 and Bruker AM-500 instruments. All other spectra (^{13}C and ^{89}Y) were recorded on a Bruker AM-500. Thermogravimetric measurements were made on a DuPont Instruments 950 thermogravimetric analyzer and mass spectral data were obtained with an upper mass limit of 900 m/e. Infrared spectra were recorded on a Perkin-Elmer Model 283 spectrometer and Nicolet Model 510P FT-IR.

Synthesis of $K[N(SiMe_3)_2]$. In a typical preparation, a 100 mL flask was charged with 5.1 g (127 mmol) of KH (obtained from Aldrich). Approximately 30 mL of freshly distilled degassed toluene was added with 25 mL (118.5 mmol) of hexamethyldisilazane (Aldrich). The reaction mixture was stirred for 12 h under dinitrogen. The mixture was then refluxed for 12 h to insure completeness of reaction. The volatiles were removed in vacuo yielding a white powder. Yield: 94%. ^1H NMR: 0.132(s) in d_8-toluene-d_8.

Synthesis of $Y[N(SiMe_3)_2]_3$. Because of the tendency[6,7] of this multistep reaction to stop at an incomplete stage of chloride substitution (i.e., to give $YCl[N(SiMe_3)_2]_2$), we give here full synthetic details. In a typical synthesis, a 200 mL flask was charged with 12.3 g (61.6 mmol) of $K[N(SiMe_3)_2]$. Approximately 40 mL of degassed THF was added. A THF slurry of YCl_3 (4.2 g, 21.5 mmol) was slowly added with stirring to the $K[N(SiMe_3)_2]$ solution. The reaction mixture was then refluxed for 24 h and reduced to dryness in vacuo. The resulting solid mixture was sublimed at approximately 20 mTorr and 150 °C for 12 h. The product was then harvested and the sublimation continued. This yielded a white crystalline solid. Yield: 50% ^1H NMR: 0.290(s) in C_6D_6.

Purification of Hacac.[8] Acetylacetone (Aldrich) was separated from acetic acid impurity as follows: 100 mL of commercial Hacac was extracted several times with several volumes of dilute KOH(aq), followed by several volumes of water. The remaining Hacac was dried over Na_2SO_4 for 12 h and then filtered into a flask and dried over P_2O_5. Finally, the Hacac was distilled under vacuum at 30 °C.

Synthesis of $[Y(acac)_3]_n$. Approximately 1.2 g (2.1 mmol) of $Y[N(SiMe_3)_2]_3$ were dissolved in a minimum amount of toluene to obtain complete dissolution. To this rapidly stirring solution, 0.7 mL (6.8 mmol) of acetylacetone was added dropwise. Immediately, the colorless solution turned a pale yellow whose intensity increased as more acetylacetone was added. Upon near-stoichiometric addition of acetylacetone, the now deep-yellow solution returned to its original colorless hue. The solution was allowed to stir for 12 h at room temperature under a slight N_2 purge.

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(1) Erasmus, C. S.; Boeyens, J. C. A. *Acta Crystallogr.* **1970**, *B26*, 1843.
(2) Leskelä, M.; Sillanpää, R.; Niinistö, L.; Tiitta, M. *Acta Chem. Scand.* **1991**, *45*, 1006.
(3) Kawaguchi, S. *Coord. Chem. Rev.* **1986**, *70*, 51.
(4) (a) Przystal, J. K.; Bos, W. G.; Liss, I. B. *J. Inorg. Nucl. Chem.* **1971**, *33*, 679. (b) Berg, E. W.; Chiang Acosta, J. J. *Anal. Chim. Acta* **1968**, *40*, 101.
(5) Cunningham, J. A.; Sands, D. E.; Wagner, W. F. *Inorg. Chem.* **1967**, *6*, 499.
(6) Evans, W. J.; Golden, R. E.; Ziller, J. W. *Inorg. Chem.* **1991**, *30*, 4963.
(7) Aspinall, H. C.; Bradley, D. C.; Hursthouse, M. B.; Sales, K. D.; Walker, N. P. C.; Hussain, B. *J. Chem. Soc., Dalton Trans.* **1989**, *4*, 623.
(8) Cartledge, G. H. *J. Am. Chem. Soc.* **1951**, *73*, 4416.

0020-1669/93/1332-0497$04.00/0

Table I. Crystallographic Data for $Y_4(OH)_2(acac)_{10}{\cdot}4C_6H_6$

chem formula	$C_{50}H_{72}O_{22}Y_4{\cdot}4C_6H_6$	space group	$P\bar{1}$
a, Å	13.606(4)	T, °C	−175
b, Å	13.951(5)	λ, Å	0.710 69
c, Å	11.366(4)	ρ_{calcd}, g cm^{-3}	1.439
α, deg	96.70(2)	μ(Mo Kα), cm^{-1}	30.3
β, deg	112.39(1)	R^a	0.0642
γ, deg	78.57(2)	$R_w{}^a$	0.0570
V, Å^3	1953.32		
Z	2		
fw	846.59		

[a] $R = \sum|F_o - F_c|\sum F_o$. [b] $R_w = [\sum w(F_o - F_c)^2/\sum wF_o{}^2]^{1/2}$. $w = 1/\sigma^2$.

After stirring, the volatiles were stripped in vacuo and the resulting off-white powder was washed with several volumes of hexanes, mp 123–125 °C. ^{1}H NMR (25 °C, C_6D_6): 1.87 (s, 6H), 5.31 (s, 1H). ^{89}Y NMR (25 °C, C_6D_6): 73.96 (s). Elemental analysis calculated for $C_{15}H_{21}O_6Y$: C, 46.63; H, 5.4; Found: C, 46.58; H, 5.42. Mass spectrum: (m/e = 672 $[Y_2(acac)_6 - Hacac]^+$, 4%); 386 $(Y(acac)_3{}^+$, 50%); 287 $(Y(acac)_2{}^+$, 100%); 205 $(Y(acac)(OH)^+$, 8%).

Synthesis of $Y_4(acac)_{10}(OH)_2$ by Adventitious Hydrolysis. A sample of anhdryous $[Y(acac)_3]_n$ was placed in a flask and dissolved in a minimum amount of hexanes and placed at −20 °C. Upon cooling, small colorless crystals precipitated. These were suitable for X-ray analysis.

Synthesis of $NH_4(acac)$. Acetylacetone (11.7 mL, 114 mmol) was added to a solution of 4.6 mL (118 mmol) of concentrated NH_4OH which was already diluted with 30 mL of distilled water. A white precipitate formed immediately. The reaction was stirred and small volumes of distilled water were added until the white solid had dissolved. This solution was then immediately used in the synthesis of $Y(acac)_3{\cdot}3H_2O$.

Synthesis of $Y(acac)_3{\cdot}3H_2O$. This synthesis is a variant on two earlier syntheses.[5,9] 4.3 g (19.0 mmol) of Y_2O_3 was partially dissolved in approximately 40 mL of dilute HCl. The pH was adjusted to 5.3 using NH_4OH. To this solution, another aqueous solution containing 12.87 g (118 mmol) of $NH_4(acac)$ was added dropwise. During the course of the reaction, the pH was constantly monitored with a glass electrode. The pH was adjusted such that it never exceeded 6.3 to prevent the formation of $Y(OH)_3$. The resulting mixture was stirred for 20 h. When filtered, the mixture yielded a white powder. This powder was dissolved in several flasks each containing 2–3 g of crude wet product and 100 mL of a mixture of approximately 80% ethanol/water. These flasks were then cooled to −20 °C and yielded colorless crystalline material after one day. Yield: 88%.

Synthesis of $Y_4(acac)_{10}(OH)_2{\cdot}4C_6H_6$. $Y(acac)_3{\cdot}3H_2O$ (0.5 g) was heated (85 °C) under vacuum for 18 h. The now slightly discolored solid was extracted into 40 mL of hexanes. After filtration, all volatiles were removed in vacuo from the hexane solution and the resulting white powder was extracted into Et_2O and then the volatiles were removed in vacuo. This white powder was then dissolved in a minimum amount of benzene. Benzene was then removed in vacuo until the cloud point, the supersaturated solution was then heated gently until complete dissolution occurred and it was allowed to slowly come to room temperature. Within 24 h, colorless crystals formed in the flask. ^{89}Y NMR (C_6D_6): 65.8 ppm. ^{1}H NMR (C_6D_6): 5.37 (intensity 1), 5.33(2), 5.30(1), 5.28(1), 1.99(6), 1.96(6), 1.94(6), 1.89(6), 1.88(12).

Table II. Fractional Coordinates[a] and Isotropic Thermal Parameters[b] for $Y_4(OH)_2(acac)_{10}{\cdot}4C_6H_6$

	x	*y*	*z*	$10B_{iso}$
Y(1)	6898(1)	3119.8(5)	895(1)	14
Y(2)	5988(1)	5872.4(5)	326(1)	14
O(3)	5644(4)	4328(3)	−391(5)	13
O(4)	5133(4)	2542(3)	−267(4)	17
C(5)	5085(6)	1705(6)	−872(7)	19
C(6)	5838(6)	865(5)	−490(7)	22
C(7)	6789(6)	790(5)	602(7)	20
O(8)	7135(4)	1517(3)	1301(5)	21
C(9)	4139(6)	1646(6)	−2103(8)	27
C(10)	7447(7)	−187(6)	961(8)	30
O(11)	7883(4)	3063(3)	3034(4)	17
C(12)	7700(6)	3287(5)	4030(7)	17
C(13)	6676(6)	3648(5)	4080(7)	19
C(14)	5694(6)	3861(5)	3048(7)	19
O(15)	5582(4)	3759(3)	1872(4)	16
C(16)	8651(6)	3168(6)	5282(7)	27
C(17)	4715(6)	4223(7)	3381(8)	29
O(18)	7483(4)	4703(3)	1509(4)	17
C(19)	8249(6)	4934(5)	2571(7)	19
C(20)	8057(6)	5556(6)	3499(7)	21
C(21)	7028(6)	6003(6)	3482(7)	22
O(22)	6200(4)	6072(4)	2469(4)	21
C(23)	9362(6)	4448(6)	2706(7)	24
C(24)	6880(7)	6410(6)	4689(8)	31
O(25)	6771(4)	2684(3)	−1166(4)	18
C(26)	7345(6)	2115(6)	−1675(7)	23
C(27)	8456(7)	1786(6)	−1075(8)	27
C(28)	9042(6)	2084(6)	200(8)	23
O(29)	8626(4)	2610(4)	912(5)	22
C(30)	6800(7)	1773(7)	−3037(9)	38
C(31)	10243(6)	1755(6)	723(8)	29
O(32)	6964(3)	5372(3)	−950(4)	17
C(33)	7894(6)	5409(5)	−892(7)	18
C(34)	8555(6)	6025(6)	−18(8)	22
C(35)	8254(6)	6676(5)	852(7)	20
O(36)	7318(4)	6811(3)	917(4)	18
C(37)	8295(6)	4742(6)	−1782(8)	28
C(38)	9019(6)	7291(6)	1784(7)	23
C(39)	3236(6)	1414(6)	3059(8)	29
C(40)	3236(6)	1784(6)	2003(7)	27
C(41)	4191(7)	1810(6)	1870(8)	30
C(42)	5153(7)	1454(6)	2783(9)	31
C(43)	5148(7)	1083(6)	3849(8)	33
C(44)	4206(7)	1058(7)	3997(7)	32
C(45)	10556(8)	1520(7)	4080(10)	42
C(46)	11534(8)	1319(7)	5089(9)	37
C(47)	11961(7)	382(7)	5419(8)	33
C(48)	11439(7)	−365(7)	4763(9)	35
C(49)	10462(7)	−158(7)	3755(9)	38
C(50)	10019(7)	777(8)	3422(9)	39
H(1)	577(5)	408(5)	−101(7)	11(14)

[a] Fractional coordinates are ×10^4 for non-hydrogen atoms and ×10^3 for hydrogen atoms. [b] Isotropic values for those atoms refined anisotropically are calculated using the formula given by Hamilton: Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609: $B_{eq} = (16\pi 2/3)\mathbf{A'BA}$.

X-ray Structure Determination of $Y_4(acac)_{10}(OH)_2{\cdot}4C_6H_6$. A crystal of suitable size was mounted in a nitrogen atmosphere glove bag using silicone grease and it was then transferred to a goniostat where it was cooled to −175 °C for characterization and data collection.[10] This was done as quickly as possible because the crystals were known to lose solvent and decompose when removed from the mother liquor. The colorless crystal was a pale milk-white by the time the transfer was complete but appeared quite stable once it had been cooled in the nitrogen vapor cold stream. A search of a limited hemisphere of reciprocal space (Table I) revealed no symmetry among the observed intensities. An initial choice of space group $P\bar{1}$ was later proven correct by the successful solution of the structure. Following complete intensity data collection (6° < 2θ < 45°) and correction for absorption, data processing gave a residual of 0.041 for the averaging of 1224 unique intensities which had been measured more than once. Four standards measured every 400 data showed no significant trends. The structure was solved using a combination of direct methods (MULTAN78) and Fourier techniques. The yttrium positions were determined from an initial *E*-map. The remaining non-hydrogen atoms and the hydrogen on the OH ligand were determined from subsequent iterations of least-squares refinement and difference Fourier calculation. Hydrogens bonded to carbon were included in fixed calculated positions with thermal parameters fixed at one plus the isotropic thermal parameter of the atom to which they were bonded. In the final cycles of refinement, the non-hydrogen atoms were varied with anisotropic thermal parameters and the OH hydrogen was varied with an isotropic thermal parameter. The largest peaks in the final difference map were yttrium residuals of 0.67 to 0.97 e/Å^3. All other residual peaks were 0.66 e/Å^3 or less. The largest hole was −1.11 e/Å^3. The results of the structure determination are shown in Tables II and III and Figures 1 and 2. Additional information is available as supplementary material.

Results

Synthesis. Our preferred method to produce $Y(acac)_3$ was to execute the synthesis under totally anhydrous conditions, rather

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(9) Stites, J. G.; McCarty, C. N.; Quill, L. L. *J. Am. Chem. Soc.* **1948**, *70*, 3142.

(10) Huffman, J. C.; Lewis, L. N.; Caulton, K. G. *Inorg. Chem.* **1980**, *19*, 2755.

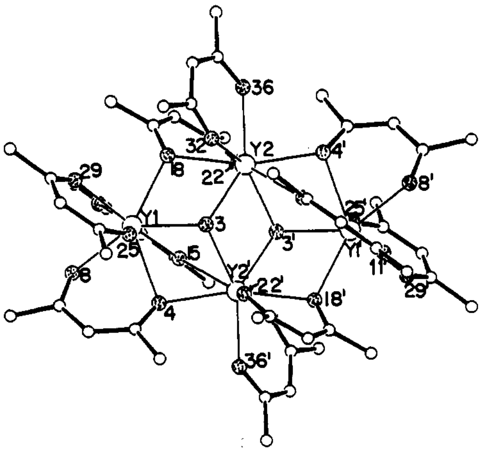

Figure 1. ORTEP drawing of the non-hydrogen atoms of $Y_4(OH)_2(acac)_{10}$, showing selected atom labeling. Oxygens are stippled, and O(3) and O(3)′ are hydroxide groups.

Table III. Selected Bond Distances (Å) and Angles (deg) for $Y_4(OH)_2(acac)_{10}$

Y(1)–O(3)	2.329(5)	Y(2)–O(3)	2.285(5)
Y(1)–O(4)	2.502(4)	Y(2)–O(3)′	2.322(5)
Y(1)–O(8)	2.271(5)	Y(2)–O(4)′	2.418(5)
Y(1)–O(11)	2.288(4)	Y(2)–O(15)′	2.620(4)
Y(1)–O(15)	2.426(5)	Y(2)–O(18)	2.392(5)
Y(1)–O(18)	2.433(5)	Y(2)–O(22)	2.331(5)
Y(1)–O(25)	2.300(5)	Y(2)–O(32)	2.284(5)
Y(1)–O(29)	2.312(5)	Y(2)–O(36)	2.292(4)
O(3)–Y(1)–O(4)	69.25(15)	O(3)–Y(2)–O(15)′	79.38(15)
O(3)–Y(1)–O(8)	141.24(16)	O(3)′–Y(2)–O(15)′	69.14(16)
O(3)–Y(1)–O(11)	133.47(17)	O(3)–Y(2)–O(18)	70.74(16)
O(3)–Y(1)–O(15)	72.57(17)	O(3)′–Y(2)–O(18)	113.57(16)
O(3)–Y(1)–O(18)	69.30(15)	O(3)–Y(2)–O(22)	108.68(17)
O(3)–Y(1)–O(25)	72.83(17)	O(3)′–Y(2)–O(22)	74.43(17)
O(3)–Y(1)–O(29)	124.04(17)	O(3)–Y(2)–O(32)	75.72(17)
O(4)–Y(1)–O(8)	72.46(16)	O(3)′–Y(2)–O(32)	137.86(17)
O(4)–Y(1)–O(11)	126.78(16)	O(3)–Y(2)–O(36)	142.10(17)
O(4)–Y(1)–O(15)	67.42(15)	O(3)′–Y(2)–O(36)	147.48(17)
O(4)–Y(1)–O(18)	135.60(15)	O(4)′–Y(2)–O(15)′	65.64(15)
O(4)–Y(1)–O(25)	72.05(16)	O(4)′–Y(2)–O(18)	148.75(16)
O(4)–Y(1)–O(29)	134.34(17)	O(4)′–Y(2)–O(22)	81.32(17)
O(8)–Y(1)–O(11)	76.21(17)	O(4)′–Y(2)–O(32)	124.40(16)
O(8)–Y(1)–O(15)	98.25(17)	O(4)′–Y(2)–O(36)	82.10(16)
O(8)–Y(1)–O(18)	149.00(16)	O(15)′–Y(2)–O(18)	145.61(15)
O(8)–Y(1)–O(25)	90.00(17)	O(15)′–Y(2)–O(22)	136.86(16)
O(8)–Y(1)–O(29)	80.16(18)	O(15)′–Y(2)–O(32)	82.07(15)
O(11)–Y(1)–O(15)	76.00(16)	O(15)′–Y(2)–O(36)	115.97(15)
O(11)–Y(1)–O(18)	74.92(16)	O(18)–Y(2)–O(22)	71.03(17)
O(11)–Y(1)–O(25)	149.45(17)	O(18)–Y(2)–O(32)	74.52(16)
O(11)–Y(1)–O(29)	78.64(17)	O(18)–Y(2)–O(36)	80.87(16)
O(15)–Y(1)–O(18)	85.57(16)	O(22)–Y(2)–O(32)	141.00(16)
O(15)–Y(1)–O(25)	133.66(15)	O(22)–Y(2)–O(36)	84.10(17)
O(15)–Y(1)–O(29)	154.18(16)	O(32)–Y(2)–O(36)	72.80(17)
O(18)–Y(1)–O(25)	109.60(16)	Y(1)–O(3)–Y(2)′	104.00(18)
O(18)–Y(1)–O(29)	83.30(17)	Y(1)–O(3)–Y(2)	112.87(19)
O(25)–Y(1)–O(29)	72.14(16)	Y(2)–O(3)–Y(2)′	110.62(20)
O(3)–Y(2)–O(3)′	69.38(20)	Y(1)–O(4)–Y(2)′	96.29(15)
O(3)–Y(2)–O(4)′	134.10(15)	Y(1)–O(15)–Y(2)′	93.08(15)
O(3)′–Y(2)–O(4)′	70.88(15)	Y(1)–O(18)–Y(2)	105.69(16)

than to remove coordinated water from a product synthesized under aqueous conditions. The method of eq 1, carried out with

$$Y[N(SiMe_3)_2]_3 + 3Hacac \rightarrow Y(acac)_3 + 3HN(SiMe_3)_2 \quad (1)$$

an 8% excess of acetylacetone and at 25 °C in toluene, proceeded smoothly to a single product. The product is soluble in benzene, toluene and, to a limited extent, even hexane. The ^1H NMR spectrum at 25 °C in C_6D_6 shows one methine and one methyl resonance. The ^{89}Y NMR spectrum in C_6D_6 is a singlet. While these observations are consistent with a six-coordinate monomeric formulation, low temperature studies suggest an aggregated (but fluxional) formula $Y_n(acac)_{3n}$. At −70 °C in toluene-d_8, both the ^1H and ^{89}Y NMR signals broaden. By −80 °C, the ^{89}Y NMR signal was broadened into the baseline. By using an 80:20 mixture of Et_2O and toluene-d_8, the ^{89}Y NMR spectrum was recorded at −105 °C. It consisted of two lines of equal intensity (96.0 and 56.3 ppm). In this solvent mixture at 25 °C, the ^{89}Y NMR spectrum had coalesced to a singlet as found in C_6D_6. Two lines of equal intensity require an even value for the degree of aggregation, n. We feel that $n = 2$ is unlikely, since *unsymmetrical* dimers are extremely rare.[1] We therefore propose $n = 4$, with an acyclic form where two Y are "inside" and two are at the ends, as the true formulation of "$Y(acac)_3$". An electron impact mass spectrum showed a strong peak for $[Y_2(acac)_5\text{-}H]^+$, as well as very weak peaks above the mass of $Y_2(acac)_6$.

Attempts at slow crystallization of $[Y(acac)_3]_n$ by cooling in hexane yielded crystals which were shown by X-ray crystallography to have empirical formula $Y_2(OH)(acac)_5$. The actual molecule is a centrosymmetric dimer of this formula, and the compound itself is obviously a product of accidental partial hydrolysis. This product was obtained in only low yield, but attracted our attention because its low solubility led to crystallization. $[Y(acac)_3]_n$ is clearly more soluble. The structure of this product differs negligibly from that shown in Figures 1 and 2, and is described in detail in the supplementary material. Since we later produced this material more rationally, and in higher yield, and determined the structure of a different composition of matter to higher precision, we will defer our discussion of the structure to a later section.

Attempted Controlled Hydrolysis of $[Y(acac)_3]_n$. Given the ease of conversion of $[Y(acac)_3]_n$ to $Y_4(acac)_{10}(OH)_2$, we anticipated that this product might be rationally produced under conditions of controlled hydrolysis (eq 2). Addition of water, in

$$4/n[Y(acac)_3]_n + 2H_2O \rightarrow Y_4(acac)_{10}(OH)_2 + 2Hacac \quad (2)$$

the amount shown in eq 2, to $[Y(acac)_3]_n$ dissolved in benzene or toluene converted about 80% of the anhydrous $[Y(acac)_3]_n$. The water was introduced as a saturated solution of the aromatic solvent. The outcome of this controlled hydrolysis was evaluated by recording the ^{89}Y NMR spectrum of the benzene-soluble material. This revealed (in addition to 20% $[Y(acac)_3]_n$) three resonances (47.1, 60.1, 67.9 ppm), in amounts which varied according to the detailed reaction conditions. None of these had the chemical shift of $Y_4(acac)_{10}(OH)_2$. If the reaction was repeated with 100% excess of H_2O and in benzene, one observes less unreacted $[Y(acac)_3]_n$, all of the above three yttrium NMR peaks, but three more peaks (65.8, 85.9 and 92.0 ppm). Control of the bimolecular hydrolysis to a single product thus appeared problematic.

"Dehydration" of $Y(acac)_3 \cdot 3H_2O$. We therefore turned to $Y(acac)_3 \cdot 3H_2O$ as an alternative potential source of $Y_4(acac)_{10}(OH)_2$. This reagent is easily accessible in a one-pot reaction from Y_2O_3 and it contains a known amount of water. The crystal structure shows two waters to be coordinated and the third to be in the lattice, but hydrogen bonded to the oxygens of coordinated water.

The reaction we hoped to carry out is represented by eq 3. Thermogravimetric analysis of this crystalline solid in flowing helium shows a first weight loss of about 7%, followed by a plateau

$$4Y(acac)_3 \cdot 3H_2O \rightarrow Y_4(acac)_{10}(OH)_2 + 2Hacac + 10H_2O \quad (3)$$

from 80 to 150 °C. The inflection point of this first weight loss is at 68 °C. Such a small weight decrease can only be due to loss of H_2O. Above 180 °C, larger percentage weight loss episodes

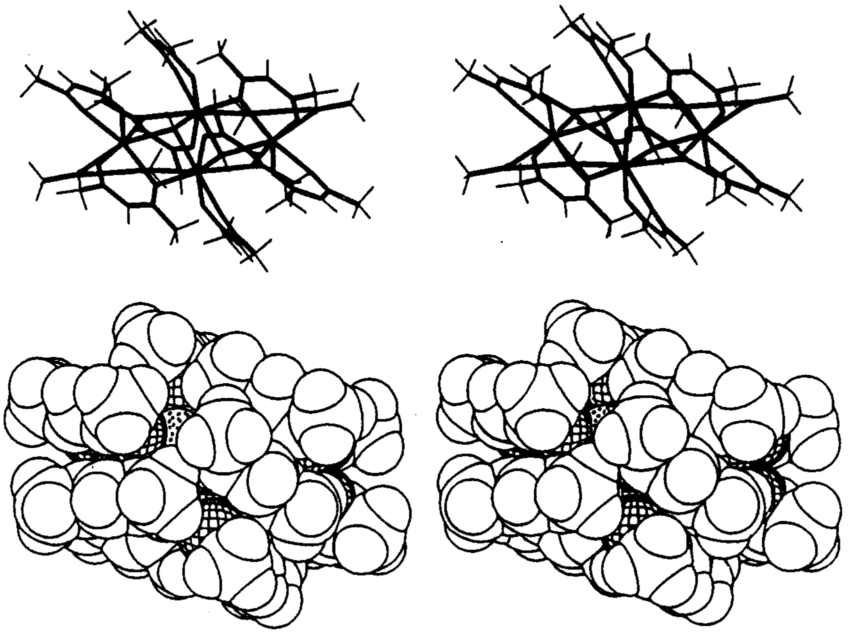

Figure 2. Stereo stick and space-filling drawings of $Y_4(OH)_2(acac)_{10}$ viewed oblique to the Y_4 plane. One of the OH hydrogens is stippled, to show its hydrocarbon-shielded environment.

occur. We therefore investigated thermolysis under vacuum of bulk crystalline solid $Y(acac)_3{\cdot}3H_2O$ at 85 °C. Following 18 h under vacuum at 85 °C, the resulting solid was extracted with hexanes. The hexane-soluble solid, after a brief wash with a small volume of Et_2O, showed an ^{89}Y NMR spectrum with a dominant signal at 65.8 ppm, a weaker signal at 67.2 ppm, and a trace ($\sim$10%) signal at 76 ppm due to $[Y(acac)_3]_n$. This reveals that "simple" dehydration of the trihydrate material to $[Y(acac)_3]_n$ can be effected, but only with extremely poor efficiency. The major product derives from acac ligand loss, and contains hydroxide. Consistent with this conclusion, mass spectral data for $Y(acac)_3{\cdot}3H_2O$ at sample temperatures near 100 °C indicate that the major ion fragments are Hacac and its subsequent fragmentation products. Therefore, the dominant process is hydrolytic loss of Hacac, and replacement of the chelate by hydroxide. The infrared spectrum of the resulting solid showed the presence of an OH group uninvolved in hydrogen bonding ($\nu_{OH} = 3603\ cm^{-1}$). Recrystallization of this solid from benzene yielded crystals which showed only the 65.8 ppm ^{89}Y NMR peak. Curiously, these crystals were a different space group from that of $Y_4(acac)_{10}(OH)_2$ obtained above. ^1H NMR studies showed these new crystals (from benzene) also contained benzene in the lattice.

A single-crystal X-ray study revealed that this composition of matter differs from that crystallized earlier by inclusion of four molecules of benzene for each $Y_4(acac)_{10}(OH)_2$ molecule. The molecule has a crystallographic center of symmetry (Figures 1 and 2). One acac ligand on each metal is wholly terminal. The remaining six acac ligands have one oxygen terminal to a metal and the other oxygen bridging that metal to a second metal. Taken together with two μ_3-OH groups (which project, respectively, above and below the Y_4 plane), each yttrium achieves a coordination number of eight. This structural type was reported recently for $Nd_4(acac)_{10}(OH)_2$.[11] A similar planar $Ln_4(\mu_2\text{-}OH)_2$ structural unit also occurs in a recently reported lanthanum-copper complex.[12] Another planar $Zn_4(\mu_3\text{-}OMe)_2$ structural core was reported for a centrosymmetric zinc alkyl compound.[13]

There is considerable dispersion of Y–O distances. The terminal distances to Y(1) vary from 2.271(5) to 2.312(5) Å, while those to Y(2) vary from 2.284(5) to 2.331(5) Å. Distances from bridging acac oxygen to Y(1) vary from 2.426(5) to 2.502(4) Å, while those to Y(2) vary from 2.392(5) to a very long 2.620(4) Å. They are thus longer than to terminal oxygens. Distances from yttrium to the μ_3-OH oxygen are intermediate, varying from 2.285(5) to 2.329(5) Å. There is noticeable (Figure 2) folding of the terminal Y(acac) rings about the O···O line, and a twisting of the carbon backbone of the bridging acac ligands.

The 500 MHz ^1H NMR spectrum of $Y_4(acac)_{10}(OH)_2{\cdot}4C_6H_6$ in C_6D_6 at 25 °C shows four methine resonances (intensity 1:2:1:1). Since the centrosymmetric structure found twice for $Y_4(acac)_{10}(OH)_2$ should display five methine singlets, we conclude from the ^1H NMR result that the molecule is stereochemically rigid, but with accidental degeneracy of two methine resonances. The ^1H NMR spectrum in the methyl region shows only five chemical shifts. Since these nuclei are more remote from the metal centers, the occurrence of accidental degeneracy is increased.

Discussion and Conclusions

The silylamide compound $Y[N(SiMe_3)_2]_3$ has the requisite reactivity to be converted completely by Hacac into $[Y(acac)_3]_n$, which has good solubility in noncoordinating solvents. While it has sufficient volatility to yield an electron impact mass spectrum, the necessary combined thermal and electron impact energies are such that major fragmentation into smaller oligomers occurs and a reliable value of *n* in the gas phase cannot be determined in that way. The volatility is certainly too low (no vacuum sublimation at 125 °C) to correspond to a monomer ($n = 1$) however. This compound is extremely sensitive to accidental hydrolysis (thus frustrating reliable solution molecular weight measurements), to form a fractional hydrolysis product of formula $Y_4(OH)_2(acac)_{10}$. This material is apparently a thermodynamic "sink", and *it* (and not $[Y(acac)_3]_n$) is thus a major product of attempted dehydration of $Y(acac)_3{\cdot}3H_2O$. The structure of $Y_4(OH)_2(acac)_{10}{\cdot}4C_6H_6$ crystallized from benzene is the same as that crystallized (from hexane) without benzene in the crystal lattice. It must be concluded that the high acidity of water coordinated to a highly electropositive metal like Y(III) promotes proton transfer to the acac ligand, with subsequent loss of Hacac by volatilization. We have calculated all O/O distances from

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(11) Poncelet, O.; Hubert-Pfalzgraf, L. G. *Polyhedron* **1989**, *8*, 2183.

(12) Blake, A. J.; Milne, P. E. Y.; Thorton, P.; Winpenny, R. E. P. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1139.

(13) Dekker, J.; Schouten, A.; Budzelaar, P. H. M.; Boersma, J.; Van der Kerk, G. J. M.; Spek, A. L.; Duisenberg, A. J. M. *J. Organomet. Chem.* **1987**, *320*, 1.

water to acac oxygens in $Y(acac)_3{\cdot}3H_2O$ and find many (i.e., more than cited in ref 5) in the range 2.71–3.00 Å, both intramolecular and intermolecular, all of which represent hydrogen bonding. There are thus ample situations structurally "prepared" to generate OH with release of Hacac. This phenomenon may be quite general. It is thus necessary to synthesize lanthanide/acac compounds by a wholly anhydrous route if a CVD precursor of constant volatility and composition, free from slow release of metal-free volatiles (e.g., H_2O and Hacac) is to be achieved. Moreover, the aggregation preferred by $[Y(acac)_3]_4$ makes it too involatile for current CVD processing methods.

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Supplementary Material Available: Tables containing full crystallographic details and anisotropic thermal parameters for $Y_4(OH)_2(acac)_{10}{\cdot}4C_6H_6$ and a full report of the structure determination of $Y_4(OH)_2(acac)_{10}$ including text describing the study and tables of crystallographic data, fractional coordinates and isotropic thermal parameters, anisotropic thermal parameters, and bond distances and angles (12 pages). Ordering information is given on any current masthead page.