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Chemistry of Yttrium Triisopropoxide Revisited. Characterization and Crystal Structure of $Y_5(\mu_5\text{-}O)(\mu_3\text{-}O^iPr)_4(\mu_2\text{-}O^iPr)_4(O^iPr)_5$

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The product isolated from the reaction of yttrium metal in refluxing 2-propanol is characterized by ^1H, ^{13}C, and ^{89}Y NMR spectra, solution molecular weight measurements, and mass spectra. Crystals grown from toluene–CH_2Cl_2 are shown by X-ray diffraction to have the composition $Y_5O(O^iPr)_{13}$. This compound crystallizes in the orthorhombic system (*Pbca*) with unit cell dimensions $a = 25.512$ (14) Å, $b = 21.549$ (12) Å, $c = 20.716$ (13) Å, and $Z = 8$ (at −156 °C). Its structure consists of a highly regular square pyramid of metals, an encapsulated (μ_5) oxo group, five terminal alkoxides, four μ_2-alkoxides, and four μ_3-alkoxides. All metals have the same coordination number with a distorted octahedral environment of oxygen ligands. The Y–O bond distances uniformly follow the pattern Y–μ_3-O > Y–μ_2-O > Y–O(terminal), and the Y–μ_5-O distances are comparable to those involving μ_3-O. The alkoxide ligands are not fluxional to intramolecular site exchange at 25 °C, but the terminal and bridging alkoxides rapidly exchange with added ^iPrOH.

Introduction

We are interested in developing new and selective low-temperature routes to solid-state materials possessing optical or electronic applications. One approach[2] to this objective begins with the synthesis of molecular species of the desired solid-state metal stoichiometry, with a complement of ligands chosen in part for their ability to be subsequently removed.

In the application of this "molecular precursor approach" to the production of the high-temperature electrical superconductor $YBa_2Cu_3O_7$, yttrium alkoxides are of interest. Such compounds were reported in the 1960s as the result of a program aimed at production of high-purity, rare-earth-metal oxides from alkoxide precursors.[3,4] Yttrium(III) isopropoxide was reported then to be the product of a remarkably simple and direct synthetic approach (eq 1) in neat alcohol. Its synthesis and reactivity has been

$$Y + {}^iPrOH \xrightarrow[\Delta]{HgCl_2} Y(O^iPr)_3 + H_2 \qquad (1)$$
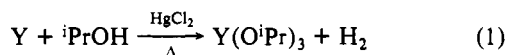
covered by several patents,[5] and the product is used for obtaining stabilized zirconia via the sol–gel process.[6]

While the yttrium isopropoxide derivative was characterized with the array of physical methods available at that time, we felt that it was essential to provide an unambiguous determination of the identity of this product as a preliminary to any major solid-state synthetic effort founded on this compound. We report here the results of such a study, which led to the structural characterization of the oxo–alkoxide $Y_5(\mu_5\text{-}O)(\mu_2\text{-}OR)_4(\mu_3\text{-}OR)_4(OR)_5$ ($R = {}^iPr$).

Experimental Section

All manipulations were routinely performed by using Schlenk tubes and vacuum-line techniques under purified argon. The solvents were purified by standard methods. ^1H and ^{13}C NMR spectra and IR spectra were run on Nicolet NT-360, Bruker WH-90, AC-200, AM-500, and IR-FTS45 spectrometers, respectively. IR spectra were obtained as Nujol mulls. ^{89}Y NMR spectra were measured at 19.608 MHz (Bruker AM-400), and ^{89}Y chemical shifts are reported with respect to YCl_3 (2 M) in D_2O and are negative to high field. Molecular weight measurements were obtained in benzene by using the Signer method.[7] Mass spectra were recorded on a R-10 Ribermag spectrometer by using chemical ionization techniques. Elemental analysis was performed by the Centre de Microalyse du CNRS.

Table I. Crystallographic Data for $Y_5O(O^iPr)_{13}$

chem formula	$C_{39}H_{91}O_{14}Y_5$	space group	*Pbca*
a, Å	25.512 (14)	T, °C	−156
b, Å	21.549 (12)	λ, Å	0.710 69 Å
c, Å	20.716 (13)	ρ_{calc}, g cm^{-3}	1.43
V, Å^3	11388.50	μ, cm^{-1}	51.2
Z	8	$R(F)$	0.0905
fw	1228.67	$R_w(F)$	0.0903

Synthesis of $Y_5O(O^iPr)_{13}$. Its synthesis was achieved according to the procedure of Mazdiyasni,[3,4] slightly modified. A 10-g (0.11-mol) sample of yttrium chips (Alfa or Aldrich) was heated at 80 °C for 1 h with 300 mL of a mixture of toluene and 2-propanol (1:1). The catalyst ($HgCl_2$ + $Hg(OAc)_2$ (1:1), 10 mg) was then added, and refluxing was maintained for 36–48 h. Following rapid filtration of the hot solution, crystallization occurred by cooling to room temperature. A second crop of crystals was obtained at −40 °C. After the crystals were dried in a vacuum at room temperature for 48 h, 20.7 g (75%) of $Y_5O(O^iPr)_{13}$ was isolated. $Y_5O(O^iPr)_{13}$ is soluble in common organic solvents, including pentane and petroleum ether, but its solubility in 2-propanol is relatively low. Anal. Calcd for $C_{39}H_{91}O_{14}Y_5$: C, 38.12; H, 7.46. Found: C, 38.21; H, 7.68. Molecular weight (C_6H_6): 1140 ± 114. MS (CI, NH_3 m/e^+, %): $Y_5(OR)_9$ or $Y_4O_2(OR)_9(OC_3H_5)$ (100%); $Y_4O(OR)_9$ (20%); Y_5O-$(OR)_7(OC_3H_5)$ or $Y_4(OR)_9$ (14%); $Y_3(OR)_8$ (20%); $Y_3(OR)_2(OC_3H_5)_3$ (80%), $Y_2O(OR)_6$ (67%), $Y_2O_2(OR)_5$ (34%), $Y_2OH(OR)_5$ (27%), $Y_2O_2(OR)_4$ (14%), $Y_2O_5C_{12}H_{30}$ (14%), $Y_2OC_{14}H_{27}$ (27%). ^1H NMR ($CDCl_3$; ppm): 1.50, 1.29, 1.05 (d, $J = 6$ Hz) (CH_3) (1:1:1.25); 4.30 (septet, $J = 6$ Hz), 4.10 (m) (CH). $^{13}C\{^1H\}$ NMR (C_6D_6); ppm): 27.7, 28.5, 29.0 (CH_3); 67.0, 67.3, 67.6 (CH); ^{89}Y NMR ($CDCl_3$; ppm): −13.2; −16.9 (1:4).

$Y_5O(O^iPr)_{13}$ can also be obtained from Y turnings and pure 2-propanol in the absence of a mercury catalyst, but the yields are poor (30%). No reaction was observed between Y turnings and methanol or *tert*-butyl alcohol, even in the presence of a mercury catalyst.

Crystallography of $Y_5O(O^iPr)_{13}$. A suitable crystal, grown from toluene–CH_2Cl_2 mixtures (1:1) at −35 °C over 48 h, was transferred to the goniostat where it was cooled to −156 °C for characterization and data collection.[8] A systematic search of a limited hemisphere of reciprocal space was carried out by using a locally developed, computer-controlled search program. The set of carefully centered reflections exhibited orthorhombic diffraction symmetry, *mmm*, and the systematic extinctions of $0kl$ for $k = 2n + 1$, $h0l$ for $l = 2n + 1$, and $hk0$ for $h = 2n + 1$ uniquely identified the space group as *Pbca* (No. 61). It was evident that the quality of the data was inferior to what we usually obtain: the general background was very high, even at high diffraction angles, and the intensities decreased steeply with the diffraction angle. The early search revealed very few strong reflections beyond $2\theta = 20°$.

Data were collected (see Table I) by using the relatively slow scan rate of 4° min^{-1}, with fixed background counts of 10 s at either end of the scan. A total of 7645 reflections (including space group extinctions and standard reflections) were collected in the range $6° < 2\theta < 40°$. Following the usual data processing and averaging of equivalent reflections,

(1) (a) Université de Nice. (b) Indiana University.
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(8) For X-ray methods, see: Huffman, J. C.; Lewis, L. N.; Caulton, K. G. *Inorg. Chem.* **1980**, *19*, 2755.
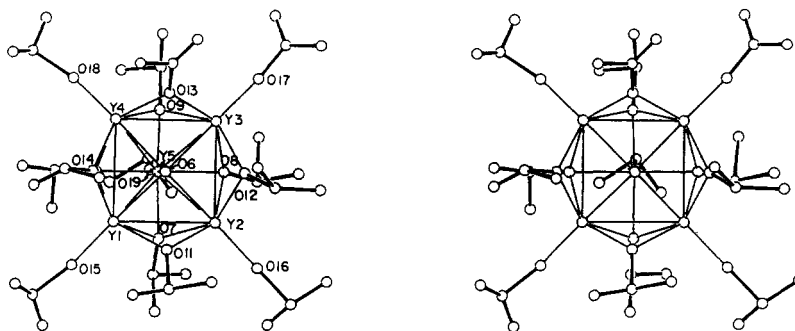
Figure 1. Stereoscopic ORTEP drawing of the non-hydrogen atoms in $Y_5O(O^iPr)_{13}$, showing atom labeling of the inner coordination sphere. Unlabeled atoms are carbon. O(10) lies behind O(14).
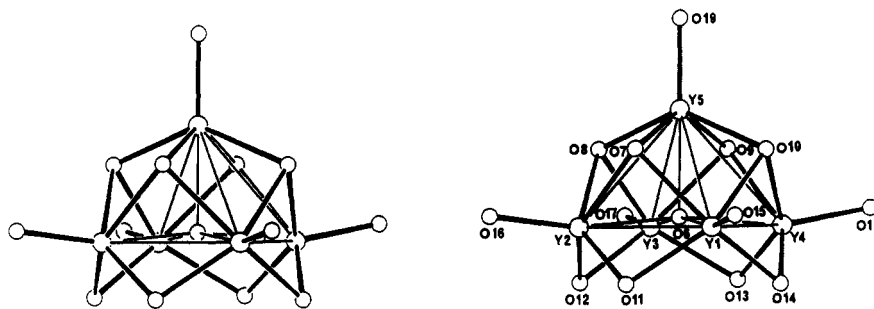

Figure 2. Stereoscopic ORTEP drawing of the Y_5O_{14} substructure, illustrating the distorted octahedral arrangement of six oxygen atoms about every metal.

a unique set of 5306 reflections remained. An uncertainty factory of 0.10 was used in the data processing. Only 4215 reflections were above zero intensity, and 1238 were considered observed by using the criterion $I > 3.0\sigma(I)$. No correction for absorption was carried out, as the faces of the crystal were poorly defined and hence difficult to identify.

The structure was solved using the usual combination of direct methods (MULTAN) and Fourier techniques. The initial best E-map showed the locations of five Y atoms as well as a few of the O atoms. Successive difference Fourier syntheses gradually revealed all of the isopropoxy groups, four of which (two μ_2, O(12) and O(14), and two terminal, O(16) and O(17)) show disordered methyl groups. Full-matrix least-squares refinement included anisotropic thermal parameters on the five Y atoms and isotropic thermal parameters on all other atoms. Refinement of the occupancy of the disordered atoms gave values close to 0.5; fixed values of 0.5 were therefore used in the final refinement model. A space-filling model reveals the considerable "looseness" around many of the isopropyl groups. For the observed reflections, this model yielded a final R of 0.0905.

The results of the structure determination are shown in Tables II and III and Figures 1 and 2. Only one set of methyl carbons is included for the four disordered isopropyl groups; parameters for the remaining methyl groups, as well as anisotropic thermal parameters and observed and calculated structure factors, are available as supplementary material. To explore the possibility that low diffraction quality was due to solvent loss, a search for "holes" in the crystal (with idealized hydrogen atoms 1.08 Å from carbon) showed the largest void to have a radius of 2.4 Å, which is too small to have held an ^iPrOH molecule. The largest peak in the final difference map was 1.01 e/A³, located 1.5 Å from Y(5).

Results

Synthesis and Characterization. The yttrium compound under study was obtained according to the procedure of Mazdiyasni.[3-5] Yttrium metal turnings or chips amalgamated with catalytic amounts of mercury salts ($HgCl_2$ or $Hg(O_2CMe)_2$) react at reflux in neat 2-propanol or 1:1 2-propanol–toluene over a period of 36–48 h. Colorless crystals were obtained in high yield (up to 75%, depending mainly on the surface characteristics of the metal) by cooling the reaction medium. Complete removal of the alcohol from these crystals—essential for obtaining reproducible and structurally diagnostic NMR spectra (see below)—requires about 48 h of drying at room temperature under dynamic vacuum (10^{-2} mmHg). This can also be achieved by sublimation (to give a microcrystalline sublimate), but sublimation is accompanied by considerable conversion to nonvolatile, poorly soluble byproducts. Disappearance in the infrared spectra of the absorption bands of coordinated ^iPrOH (3125 (ν_{OH}), 1070, 891, 886, 670 cm^{-1}) gave

spectra identical with those reported previously for "$Y(O^iPr)_3$".

Microanalytical data showed carbon and hydrogen contents reproducibly and significantly lower than required for a [Y-$(O^iPr)_3]_n$ formula, independent of the procedure (temperature) used for the elimination of the residual 2-propanol in the drying process. This has also sometimes been observed by Mazdiyasni. Since the resulting product could be contaminated by trace amounts (ppm) of mercury, which could also preclude its potential use for access to advanced materials by chemical vapor-phase decomposition techniques, its synthesis in the absence of such a catalyst has been considered. Attack of Y turnings by refluxing in neat 2-propanol is possible, although tedious, but the yields are poor ($\sim$30%) even after longer refluxing times ($\sim$4 days). The same product could be isolated (but in reduced yield) after 24 h of sonication of yttrium metal (with Hg^{2+} catalyst) in 2-propanol (reaction temperature $\sim$55 °C).

The ^1H NMR spectrum of the product at room temperature is clearly too complex for the simple monomeric formulation $Y(O^iPr)_3$ or for the dimeric one reported by Mazdiyasni.[4] One can resolve (90 and 500 MHz in $CDCl_3$ or C_6D_6) three methyl resonances displaying comparable intensities as well as two methine resonances. $^{13}C\{^1H\}$ NMR spectra are in agreement with these observations and show three resonances for both the methine and the methyl groups.

An isopiestic ("Signer method") molecular weight determination at 25 °C in benzene gave a value of 1140 ± 10%, compared to calculated values of 1064 for $n = 4$ and 1330 for $n = 5$ in [Y-$(O^iPr)_3]_n$. The mass spectrum established that this tetra- or pentanuclear species is maintained in the gas phase, since fragments such as $Y_5(OR)_9^+$ or $Y_4O_2(OR)_9(OC_3H_5)^+$ account for the highest mass peak ($m/e^+ = 976$ (100%)).

Yttrium is a NMR-active nucleus with $I = {}^1/_2$ and 100% natural abundance; additional information might therefore be gained by ^{89}Y NMR. The ^{89}Y NMR spectrum of the compound is indeed quite informative, being composed of two sharp signals of relative intensity close to 1:4 and separated by less than 5 ppm; the less intense resonance is clearly broader than the more intense one, perhaps as a result of unresolved Y/Y' spin–spin coupling. Although ^{89}Y NMR data remain scarce,[9] the small difference in

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Table II. Fractional Coordinates and Isotropic Thermal Parameters[a] for $Y_5O(O^iPr)_{13}$

atom	10^4x	10^4y	10^4z	$10B_{iso}$, Å^2
Y(1)	7892 (3)	3364 (2)	1653 (4)	44
Y(2)	9183 (3)	3122 (3)	1754 (3)	44
Y(3)	9248 (3)	4070 (3)	3001 (4)	56
Y(4)	7973 (3)	4328 (3)	2900 (3)	48
Y(5)	8742 (3)	4617 (3)	1562 (4)	52
O(6)	8600 (15)	3783 (15)	2263 (17)	41 (9)
O(7)	8640 (16)	3696 (16)	995 (18)	51 (10)
O(8)	9494 (16)	4149 (19)	1896 (21)	69 (12)
O(9)	8715 (17)	4915 (20)	2565 (22)	76 (12)
O(10)	7866 (13)	4464 (13)	1755 (16)	28 (8)
O(11)	8428 (13)	2529 (16)	1747 (17)	42 (9)
O(12)	9461 (14)	3083 (17)	2757 (18)	49 (10)
O(13)	8542 (18)	4043 (20)	3641 (23)	82 (12)
O(14)	7521 (15)	3446 (16)	2621 (17)	39 (9)
O(15)	7356 (16)	3150 (17)	996 (19)	53 (11)
O(16)	9723 (10)	2675 (21)	1171 (24)	78 (13)
O(17)	9830 (18)	4451 (19)	3514 (23)	75 (12)
O(18)	7472 (19)	4936 (24)	3266 (24)	96 (13)
O(19)	8858 (19)	5360 (24)	984 (25)	100 (14)
C(20)	8644 (29)	3686 (29)	272 (31)	55 (15)
C(21)	9143 (33)	3909 (34)	65 (38)	98 (18)
C(22)	8558 (27)	3008 (31)	87 (31)	69 (16)
C(23)	10015 (25)	4314 (28)	1539 (33)	58 (16)
C(24)	10456 (28)	3981 (32)	1942 (36)	83 (18)
C(25)	10146 (32)	5035 (39)	1820 (42)	119 (20)
C(26)	8851 (30)	5666 (39)	2801 (40)	105 (20)
C(27)	8432 (28)	6046 (31)	2452 (34)	83 (17)
C(28)	8763 (32)	5586 (38)	3563 (40)	116 (20)
C(29)	7420 (22)	4878 (23)	1456 (26)	29 (13)
C(30)	6912 (30)	4671 (32)	1743 (40)	100 (18)
C(31)	7461 (34)	4834 (36)	738 (42)	114 (21)
C(32)	8349 (27)	1855 (29)	1507 (32)	68 (16)
C(33)	7838 (26)	1716 (27)	1535 (32)	62 (15)
C(34)	8801 (28)	1519 (31)	1900 (36)	90 (18)
C(35)	9695 (56)	2388 (63)	3017 (72)	239 (43)
C(36)	10334 (53)	2465 (63)	2876 (69)	77 (28)
C(37)	9372 (49)	2236 (55)	3576 (58)	63 (24)
C(38)	8482 (44)	3925 (47)	4341 (57)	143 (26)
C(39)	8002 (38)	3772 (40)	4497 (44)	116 (21)
C(40)	8787 (52)	4040 (61)	4726 (65)	210 (42)
C(41)	7051 (43)	3170 (46)	2919 (53)	132 (24)
C(42)	7366 (27)	2579 (34)	3211 (37)	87 (17)
C(43)	6659 (62)	3151 (65)	2638 (73)	92 (33)
C(44)	6877 (49)	3084 (54)	478 (64)	168 (33)
C(45)	6525 (32)	2791 (34)	959 (37)	105 (19)
C(46)	7022 (52)	2869 (59)	21 (68)	217 (34)
C(47)	10149 (49)	2282 (53)	731 (57)	151 (29)
C(48)	10614 (50)	2414 (57)	1052 (59)	54 (25)
C(49)	9853 (78)	2210 (91)	396 (93)	329 (65)
C(50)	10198 (45)	4749 (50)	3934 (55)	150 (28)
C(51)	10554 (32)	4332 (37)	4248 (39)	114 (20)
C(52)	10153 (63)	5317 (82)	4072 (83)	98 (38)
C(53)	7007 (46)	5470 (52)	3411 (57)	174 (28)
C(54)	6651 (44)	5162 (50)	3658 (57)	176 (31)
C(55)	7245 (42)	5916 (49)	3692 (53)	170 (28)
C(56)	8995 (38)	5992 (44)	674 (49)	131 (24)
C(57)	8548 (41)	6055 (45)	177 (49)	163 (25)
C(58)	9319 (40)	5765 (48)	165 (52)	171 (28)
C(59)	9697 (78)	2731 (76)	3597 (85)	114 (41)
C(60)	10049 (52)	2694 (52)	3172 (63)	49 (24)
C(61)	7154 (81)	3357 (88)	3499 (101)	169 (40)
C(62)	10410 (56)	2066 (64)	1342 (69)	85 (33)
C(63)	10331 (53)	5341 (66)	3673 (67)	72 (28)

[a] Isotropic values for those atoms refined anisotropically are calculated by using the formula given by: Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609.

chemical shift between the two resonances suggests similar environments (e.g., coordination number) of the two types of nonequivalent metals.

X-ray Diffraction Study. The above data may be understood on the basis of the results of a single-crystal X-ray diffraction structure determination, which reveals the elemental composition to be erroneously established in earlier work. All crystals we have produced are of marginal diffraction quality. The X-ray study

Table III. Selected Bond Distances (Å) and Angles (deg) for $Y_5O(O^iPr)_{13}$

	Y–O(terminal)	Y–μ_2O	Y–μ_3O	Y–μ_5O(6)
Y(1)	O(15) 1.98 (4)	O(11) 2.27 (3); O(14) 2.22 (4)	O(7) 2.45 (4); O(10) 2.38 (3)	2.38 (4)
Y(2)	O(16) 2.07 (5)	O(11) 2.31 (3); O(12) 2.20 (4)	O(7) 2.43 (4); O(8) 2.37 (4)	2.31 (4)
Y(3)	O(17) 2.00 (5)	O(12) 2.25 (4); O(13) 2.24 (5)	O(8) 2.38 (4); O(9) 2.45 (4)	2.33 (4)
Y(4)	O(18) 1.98 (5)	O(13) 2.20 (5); O(14) 2.30 (4)	O(9) 2.38 (4); O(10) 2.41 (3); Av 2.41	2.39 (4)
Y(5)	O(19) 2.02 (5)		O(7) 2.32 (4); O(8) 2.27 (4); O(9) 2.18 (5); O(10) 2.30 (3)	2.34 (3)
av	2.01	2.25	2.27	2.35

Y–Y Bond Distances

Y(1)–Y(2)	3.34 (1)	Y(5)–Y(2)	3.44 (1)
Y(1)–Y(4)	3.32 (1)	Y(5)–Y(4)	3.46 (1)
Y(2)–Y(3)	3.30 (1)	Y(5)–Y(3)	3.46 (1)
Y(3)–Y(4)	3.31 (1)	Y(5)–Y(1)	3.47 (1)
av	3.317	av	3.454

Bond Angles

Y(2)–Y(5)–Y(4)	85.63 (24)	O(9)–Y(4)–O(18)	105.9 (18)
Y(2)–Y(5)–Y(3)	57.16 (23)	O(10)–Y(4)–O(13)	142.8 (15)
Y(2)–Y(5)–Y(1)	57.87 (23)	O(10)–Y(4)–O(14)	78.2 (12)
Y(4)–Y(5)–Y(3)	57.16 (24)	O(10)–Y(4)–O(18)	102.9 (17)
Y(4)–Y(5)–Y(1)	57.34 (23)	O(13)–Y(4)–O(14)	106.0 (14)
Y(3)–Y(5)–Y(1)	85.42 (24)	O(13)–Y(4)–O(18)	110.1 (19)
Y(2)–Y(1)–Y(4)	89.33 (24)	O(14)–Y(4)–O(18)	108.6 (17)
O(6)–Y(1)–O(7)	66.1 (12)	O(6)–Y(5)–O(7)	68.9 (12)
O(6)–Y(1)–O(10)	66.3 (11)	O(6)–Y(5)–O(8)	66.4 (14)
O(6)–Y(1)–O(11)	78.3 (12)	O(6)–Y(5)–O(9)	68.2 (14)
O(6)–Y(1)–O(14)	79.4 (13)	O(6)–Y(5)–O(10)	68.3 (12)
O(6)–Y(1)–O(15)	167.1 (14)	O(6)–Y(5)–O(19)	177.8 (17)
Y(1)–Y(2)–Y(3)	90.07 (24)	O(7)–Y(5)–O(8)	82.5 (15)
O(6)–Y(2)–O(7)	67.4 (12)	O(7)–Y(5)–O(9)	137.0 (14)
O(6)–Y(2)–O(8)	65.4 (14)	O(7)–Y(5)–O(10)	81.7 (13)
O(6)–Y(2)–O(11)	78.9 (12)	O(7)–Y(5)–O(19)	113.2 (17)
O(6)–Y(2)–O(12)	78.4 (13)	O(8)–Y(5)–O(9)	82.4 (16)
O(6)–Y(2)–O(16)	168.6 (15)	O(8)–Y(5)–O(10)	134.7 (13)
O(7)–Y(2)–O(8)	78.2 (13)	O(8)–Y(5)–O(19)	114.1 (18)
O(7)–Y(2)–O(11)	78.6 (13)	O(9)–Y(5)–O(10)	81.0 (14)
O(7)–Y(2)–O(12)	144.5 (13)	O(9)–Y(5)–O(19)	109.7 (18)
O(7)–Y(2)–O(16)	103.8 (16)	O(10)–Y(5)–O(19)	111.1 (16)
O(8)–Y(2)–O(11)	142.7 (13)	Y(1)–O(6)–Y(2)	90.7 (12)
O(8)–Y(2)–O(12)	79.0 (14)	Y(1)–O(6)–Y(3)	169.8 (17)
O(8)–Y(2)–O(16)	106.5 (17)	Y(1)–O(6)–Y(4)	88.3 (13)
O(11)–Y(2)–O(12)	104.7 (13)	Y(2)–O(6)–Y(3)	94.5 (12)
O(11)–Y(2)–O(16)	107.1 (16)	Y(2)–O(6)–Y(3)	90.4 (13)
O(12)–Y(2)–O(16)	108.6 (17)	Y(2)–O(6)–Y(4)	170.8 (17)
Y(2)–Y(3)–Y(4)	90.33 (25)	Y(2)–O(6)–Y(5)	95.2 (13)
O(6)–Y(3)–O(8)	64.9 (14)	Y(3)–O(6)–Y(4)	88.9 (12)
O(6)–Y(3)–O(9)	64.0 (13)	Y(3)–O(6)–Y(5)	95.4 (13)
O(6)–Y(3)–O(12)	76.9 (13)	Y(4)–O(6)–Y(5)	94.0 (12)
O(6)–Y(3)–O(13)	79.2 (14)	Y(1)–O(7)–Y(2)	86.3 (12)
O(6)–Y(3)–O(17)	168.8 (16)	Y(1)–O(7)–Y(5)	92.2 (14)
O(8)–Y(3)–O(9)	74.8 (14)	Y(2)–O(7)–Y(5)	92.5 (14)
O(8)–Y(3)–O(12)	77.7 (14)	Y(2)–O(8)–Y(3)	87.9 (15)
O(8)–Y(3)–O(13)	141.6 (16)	Y(2)–O(8)–Y(5)	95.4 (15)
O(8)–Y(3)–O(17)	106.6 (17)	Y(3)–O(8)–Y(5)	95.9 (16)
O(9)–Y(3)–O(12)	138.9 (15)	Y(3)–O(9))–Y(4)	86.5 (14)
O(9)–Y(3)–O(13)	77.9 (16)	Y(3)–O(9)–Y(5)	96.7 (16)
O(9)–Y(3)–O(17)	107.6 (16)	Y(4)–O(9)–Y(5)	98.5 (17)
O(12)–Y(3)–O(13)	107.7 (15)	Y(1)–O(10)–Y(4)	87.9 (10)
O(12)–Y(3)–O(17)	109.1 (16)	Y(1)–O(10)–Y(5)	95.8 (12)
O(13)–Y(3)–O(17)	107.1 (17)	Y(4)–O(10)–Y(5)	94.6 (12)
Y(1)–Y(4)–Y(3)	90.26 (24)	Y(1)–O(11)–Y(2)	93.7 (13)
O(6)–Y(4)–O(9)	64.3 (13)	Y(2)–O(12)–Y(3)	95.7 (14)
O(6)–Y(4)–O(10)	65.8 (11)	Y(3)–O(13)–Y(4)	96.4 (19)
O(6)–Y(4)–O(13)	78.8 (14)	Y(1)–O(14)–Y(4)	94.5 (14)
O(6)–Y(4)–O(14)	77.9 (13)	Y(1)–O(15)–C(44)	171 (5)
O(6)–Y(4)–O(18)	166.1 (17)	Y(2)–O(16)–C(47)	177 (5)
O(9)–Y(4)–O(10)	74.8 (14)	Y(3)–O(17)–C(50)	173 (6)
O(9)–Y(4)–O(13)	80.1 (16)	Y(4)–O(18)–C(53)	168 (5)
O(9)–Y(4)–O(14)	139.9 (14)	Y(5)–O(19)–C(56)	168 (5)

(Figure 1) shows the compound to be in fact $Y_5O(O^iPr)_{13}$, molecular weight 1228, composed of a highly regular square-based pyramidal arrangement of five Y(III) centers, with a single O^{2-} ligand displaced 0.20 Å from the plane of the four basal Y centers toward the apical Y(5). The alkoxide ligands are of three structural types, four (O(7)–O(10)) triply bridging, four (O-

(11)–O(14)) doubly bridging, and five (O(15)–O(19)) terminal. The ^{1}H NMR results (*three* methyl doublets) can thus be rationalized by assuming accidental degeneracy of the five terminal alkoxides, which are in two environments (i.e., attached to either apical or to basal Y centers). We assign the terminal O^{i}Pr methyl proton resonance to the most intense signal, the upfield one, which is always observed to be unusually broad (see below).

The Y$_5$ square pyramid is highly regular, with the basal/basal separation (mean value 3.317 Å) shorter than the apical/basal separation (mean value 3.454 Å). The μ^2-OR groups link basal metals, and each μ_3-OR group links two basal to one apical yttrium. The Y–O bond distances uniformly follow the pattern Y–μ_3-O > Y–μ_2-O > Y–O(terminal). The μ_3-O-Y distances to the apical Y (2.18–2.32 Å) are considerably shorter than those of the basal metals (2.37–2.45 Å). The Y–μ_5-O distances are comparable to those involving μ_3-O. Both Y–O(terminal) and Y–μ_2-O bond lengths are significantly shorter than the sum of the covalent radii (2.35 Å). The placement of alkoxide and oxo ligands surrounds every metal with a distorted octahedron of oxygen ligands, and thus all metals have the same coordination number.

The region below the basal Y$_4$ plane is occupied to a considerable degree by folding of the μ_2-OR groups below that plane. Thus, while terminal oxygens O(15)–O(18) are 0.21–0.33 Å above this Y$_4$ plane, the μ_2 oxygens O(11)–O(14) lie 1.18–1.28 Å below it. Another measure of this downward fold of the μ^2 oxygens is given by the dihedral angles between the planes Y(apical)/Y-(basal)/Y(basal) and Y(basal)/Y(basal)/μ_2-O; these are all within 4° of being coplanar.

Angles Y–O–C to terminal ligands are nearly linear (168 (5)–177 (5)°) (Figure 1). These angles, and also the Y–O(terminal) distances, are quite comparable to those in Y$_3$-(O^{t}Bu)$_8$Cl(THF)$_2$[10] or in monomeric Y(2,6-^{t}Bu$_2$phenoxide)$_3$.[11] The sum of angles about each μ_2-O center ranges from 352.7 to 359.7°, indicating planarity with the three attached atoms.

The same square-pyramidal Y$_5$ geometry found in Y$_5$O(O^{i}Pr)$_{13}$ is also adopted in (η^5-Cp)$_5$Y$_5$O(OMe)$_8$.[12] The distribution of OMe ligands, four μ_2 and four μ_3, duplicates that reported here. The five η^5-Cp ligands play the role of the five terminal O^{i}Pr groups reported here and thus provide greater steric shielding of Y than in Y$_5$O(O^{i}Pr)$_{13}$. Lengths of analogous bonds in these two molecules are very similar.

Chemical Reactivity. Although every yttrium is six-coordinate in Y$_5$O(O^{i}Pr)$_{13}$, it is at first surprising that there is no evidence (^{1}H NMR, CDCl$_3$) for reaction upon addition of a large excess (up to 25 mol/Y$_5$ unit) of THF, MeOC$_2$H$_4$OMe, or pyridine. However, examination of a space-filling model shows the Y$_5$O$_{14}$ core to be totally shielded by a layer of isopropyl groups.

The ^{1}H NMR spectrum of Y$_5$O(O^{i}Pr)$_{13}$ is, by contrast, extremely sensitive to the presence of small (substoichiometric) amounts of added ^{i}PrOH, a feature that complicates establishing the presence of this species by ^{1}H NMR. With addition of 1 mol of ^{i}PrOH to 1 mol Y$_5$O(O^{i}Pr)$_{13}$ in CDCl$_3$, the most upfield methyl doublet and methine septet broaden.[13] Further addition of ^{i}PrOH leads to the coalescence of the two upfield doublets. No separate signals for free alcohol are seen at room temperature. We attribute this to rapid exchange of free alcohol with the terminal and bridging alkoxides in the cluster via a proton transfer mechanism. Exchange involving the terminal groups (most basic oxygen) is faster than that involving the bridging one. With further addition of ^{i}PrOH, the coalesced terminal and bridging YO^{i}Pr resonances move further upfield with additional increase in intensity. The ^{13}C spectra are consistent with the ^{1}H data. No irreversible

transformation of Y$_5$O(O^{i}Pr)$_{15}$ is caused by ^{i}PrOH, since Y$_5$O-(O^{i}Pr)$_{13}$ can be recovered from such solutions.

Our ^{1}H NMR results, particularly the bimolecular O^{i}Pr/HO^{i}Pr exchange with the two upfield methyl doublets, are in agreement with previous ^{1}H NMR assignments on yttrium alkoxides.[10] More important is the conclusion that there is no rapid intramolecular O^{i}Pr site exchange that would produce spectra which obscure accurate structural conclusions.

Discussion

The isolation of an oxo species from the reaction of alcohol with yttrium metal was not anticipated in previous reports of this reaction. Isolation of polymetallic oxo alkoxides by reaction of the metal with 2-propanol is, however, not limited to yttrium and has also been observed for lanthanum and neodymium.[14] Deoxygenation of alcohol by these highly oxophilic metals[15] and the low-valent intermediates resulting from the evolution of the metal from oxidation state 0 to oxidation state 3 might account for such observations. On the other hand, the workup procedure, especially the removal of the alcohol, could lead to the formation of a polymetallic oxo species by elimination of diisopropyl ether.[16] Since the isolation of the oxo alkoxide in high yield is reproducible, its formation here by "accidental" hydrolysis is less probable. ^{1}H NMR spectra of the crude product (solid obtained by vacuum removal of all solvent following 48 h of reflux) show several species other than Y$_5$O(O^{i}Pr)$_{13}$ (CH$_3$ resonances ranging from 1.25 to 1.91 ppm in CDCl$_3$), but the presence of additional alcohol precludes an unequivocal conclusion concerning the presence of Y$_5$O(OR)$_{13}$. Comparison of the reactivity of the crude product and of Y$_5$O(OR)$_{13}$ was therefore undertaken. Reaction with excess of aluminum trisisopropoxide in refluxing toluene–2-propanol medium was carried out for both materials. The heterometallic alkoxide Y(Al(O^{i}Pr)$_4$)$_3$ (characterized by microanalysis and mass spectra) was isolated (by fractional distillation) from the yttrium(III) species in situ (i.e., the toluene–^{i}PrOH reaction solution from Y chips *without* isolation of any solid). By contrast, no reaction was observed between (Al(O^{i}Pr)$_3$)$_n$ and Y$_5$O(O^{i}Pr)$_{13}$. The obtention of the previously described[17] Y(Al(O^{i}Pr)$_4$)$_3$ in high yield (up to 70% with respect to the amount of metal consumed) suggests that non-oxo species are predominant in the initial reaction solution and that the formation of the oxo cluster Y$_5$O-(OR)$_{13}$ results mainly from the structural modifications induced by the removal of the ^{i}PrOH ligands in order to achieve the most favored coordination number of six for yttrium centers in alkoxide derivatives.

The structurally characterized products from reactions of YCl$_3$ with MOR (M = Li, Na, R = ^{t}Bu) reported to date show retention of halide ligands (Y$_3$(O^{t}Bu)$_8$Cl(THF)$_2$) or (when M = Li) correspond to the anionic yttrium aggregate Y$_4$O(O^{t}Bu)$_{10}$Cl$_2^{2-}$ to which Li$^+$ counterions are ion-paired. The prevalence in these compounds of a building block composed of a Y$_3$ triangle capped by μ_3-O and μ_3-Cl or μ_3-O^{t}Bu groups has been emphasized.[10] We suggest that an alternate unifying view of these compounds, together with (η^5-Cp)$_5$Y$_5$O(OMe)$_8$ and Y$_5$O(O^{i}Pr)$_{13}$ is that all are Y$_n$ fragments of an octahedron, which always ($n > 3$) embraces an oxo ligand.
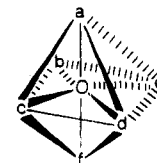
Thus, the Y$_3$ compounds have a–c occupied, Y$_4$O(O^{t}Bu)$_{10}$Cl$_2^{2-}$

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has a–d occupied, and the two Y_5 compounds have a–e occupied. To go beyond mere geometric description, and to understand the stability of these octahedral fragments, note that every triangular Y_3 face is capped by a monoanionic μ_3 ligand (Cl^- or OR^-). This makes the unifying feature of all observed structures the achievement of coordination number six for yttrium,[18] generally as a (distorted) octahedron. In this context, the (surprising!) incorporation of an oxo ligand is most efficient and compliant since it can be three-coordinate, four-coordinate or five-coordinate[19] and thus can serve to complete the favored coordination number of three, four, or even five yttrium centers.

The lack of a suitable cation under the conditions of eq 1 probably favors the formation of molecular (i.e., uncharged) reaction products; molecular reactants favor production of molecular (i.e., uncharged) reaction products. Thus, complete encapsulation of oxygen, to give $Y_6O(\mu_2\text{-}OR)_{12}(OR)_6^{2-}$, is perhaps not observed in eq 1 due in part to lack of a suitable partner cation.

The problem of achieving coordination number six in a molecular species is more readily accomplished for tetravalent metals (e.g., $U_3O(O^tBu)_{10}$,[20] $Zr_3S(S^tBu)_{10}$,[21] and $Mo_3O(OCH_2^tBu)_{10}$[22]) than for trivalent metals, since fewer anionic ligands are available in the latter case. One solution to this problem for trivalent metals is to aggregate more than three metals into a closed polyhedral fragment. In this way, the ratio of bridging to terminal ligands increases, thereby increasing the coordination number of each metal. The tolerance of O^{2-} to bind simultaneously a large number of metals also favors its incorporation.

The hypothesis that it is the yttrium coordination number that dictates product stoichiometry (identity) quite naturally explains the retention of two THF molecules in two isomers of $Y_3Cl(O^tBu)_8(THF)_2$ and in $La_3(O^tBu)_9(THF)_2$. This hypothesis predicts that a tetrahedron is an unsuitable polyhedron for a $Y_4(\mu_4\text{-}O)$ cluster since $(YOR)_4O(\mu_2\text{-}OR)_6$ has only five-coordinate yttrium. It likewise rationalizes why the reported Y_4O species is a "butterfly" and not planar (inefficient use of oxide ligand and its orbitals) as well as why it retains two chloride ligands: hypothetical $(YO^tBu)_4O(\mu_2\text{-}O^tBu)_4(\mu_3\text{-}O^tBu)_2$ would have two five-coordinate metal centers (at the "wingtips"), each of which is observed to bind one chloride.

A final question revolves around why the synthesis reported here does not yield a stable $Y_3O(O^iPr)_7(^iPrOH)_3$, structural unit similar to that of $Y_3Cl(O^tBu)_8(THF)_2$. We suggest that this is a combination of the more appropriate size and greater donor character of O vs Cl, and the smaller size of O^iPr with respect to O^tBu. The occurrence of a $Y_5O(OR)_8$ core both in this synthesis and from the reaction of KOMe·MeOH with $(\eta^5\text{-}Cp)_2YCl(THF)$[12] suggests special stability for this structural unit. The solubility of $Y_5O(OR)_{13}$, as well as the lability of the alkoxide ligands, allows its use as molecular precursors for multicomponent yttrium oxide materials by hydrolysis.[23]

Supplementary Material Available: Anisotropic thermal parameters (Table SI) and complete bond lengths and angles (Table SII) (7 pages); tables of observed and calculated structure factors (4 pages). Ordering information is given on any current masthead page.

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Structural Origin of Semiconducting Properties of the Molybdenum Red Bronzes $A_{0.33}MoO_3$ (A = K, Rb, Cs, Tl)

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Tight-binding band structure calculations were performed on the molybdenum red bronzes $Cs_{0.33}MoO_3$ and $Tl_{0.33}MoO_3$ to examine whether they are regular semiconductors or Mott insulators. Our calculations show that these red bronzes have a band gap and that their valence and conduction bands are as wide as those calculated for the blue bronze $K_{0.3}MoO_3$, which is a metal at room temperature. Thus, the red bronzes $A_{0.33}MoO_3$ (A = K, Rb, Cs, Tl) are not Mott insulators but regular semiconductors. Our analysis of the t_{2g}-block band orbitals reveals that the band gap of the red bronzes occurs as a direct consequence of the O–Mo···O alternations in their MoO_6 octahedra.

Molybdenum bronzes refer to a class of solid oxide phases of composition $A_xMo_yO_z$, where A is an alkali metal or Tl, and exhibit intense color and metallic luster. Recently, physical properties of several molybdenum bronzes have extensively been studied in connection with the charge density wave phenomenon arising from their low-dimensional metallic character.[1–3] In the molybdenum bronze, alkali metal or Tl donates its valence electron to the transition metal, so that the nature of its low-lying d-block bands determines whether the bronze is a metal or a semiconductor. Alkali-metal molybdenum oxides are classified into three

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