Synthesis of the First Bimetallic Barium Yttrium Oxo Alkoxide: Crystal Structure of $[Y_4Ba_2(\mu_6\text{-}O)(\mu_3\text{-}OEt)_8(dpm)_6]$ [dpm = Bu^{t}C(O)CHC(O)Bu^t]

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The compound $[Y_4Ba_2(\mu_6\text{-}O)(\mu_3\text{-}OEt)_8(dpm)_6]$ [dpm = Bu^{t}C(O)CHC(O)Bu^t] is obtained by mixing, in the presence of dpmH, a solution of yttrium oxo isopropoxide in toluene with a solution resulting from the reaction of Ba metal with Pr^{i}OH–EtOH; its crystal structure consists of an oxygen-centred octahedron built up from two barium and four yttrium atoms connected by eight triply bridging ethoxy groups, each of which is chelated by a terminal dpm ligand.

Heterometallic alkoxides are attractive molecular precursors to multimetallic oxide materials. They are useful for applications in sol–gel and MOCVD (metal organic chemical vapour deposition) processes because they are highly soluble and frequently obtainable through simple mixing of the homometallic species.[1] Moreover, they can offer a desired metal stoichiometry at a molecular level and a single-source precursor, which may increase the quality of the final material. The discovery of ceramic superconductors[2,3] has prompted us to research new bimetallic precursors of Ba, Y and Cu. There is very little structural data for heterometallic alkoxides of these elements; only recent molecular structures including $[Ba_2Cu_2(OR)_4(acac)_4{\cdot}2HOR]$ (Hacac = pentane-2,4-dione) (R = CH_2CH_2OMe),[4] $[Y_2Cu_8(\mu\text{-}PyO)_{12}(\mu\text{-}Cl)_2(\mu_4\text{-}O)_2(NO_3)_4(H_2O)_2{\cdot}2H_2O]$ (PyOH = 2-hydroxypyridine)[5] and $[Ba\{Cu[OCMe(CF_3)_2]_3\}_2]$[6] are known. We report here the synthesis and the characterization, including the X-ray structure, of $[Y_4Ba_2(\mu_6\text{-}O)(\mu_3\text{-}OEt)_8(dpm)_6]$ **1** (Fig. 1). It is to our knowledge, the first crystallographically characterized bimetallic barium yttrium alkoxide.

Complex **1** was obtained by mixing at reflux temperature, a solution of yttrium oxo isopropoxide in toluene with a solution resulting from the dissolution of barium metal in a hot mixture of Pr^{i}OH–EtOH (35 ml : 5 ml), in the presence of the chelating ligand dipivaloylmethane (dpmH).† Whatever the stoi-

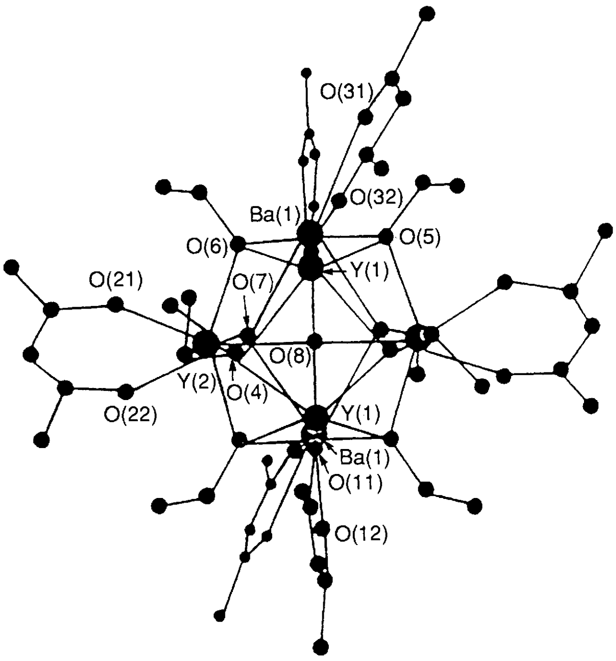

Fig. 1 Atomic numbering scheme of $Y_4Ba_2(\mu_6\text{-}O)(\mu_3\text{-}OEt)_8(dpm)_6$ with the terminal methyl groups of the dpm ligand omitted for clarity. The metal–oxygen distances (Å) are: Y(1)–O(8) 2.363(3), Y(1)–O(5) 2.322(17), Y(1)–O(6) 2.317(18), Y(1)–O(7) 2.301(17), Y(1)–O(4) 2.329(18), Y(1)–O(11) 2.282(20), Y(1)–O(12) 2.328(20), Y(2)–O(8) 2.378(3), Y(2)–O(4) 2.308(19), Y(2)–O(5) 2.315(18), Y(2)–O(6) 2.329(18), Y(2)–O(7) 2.325(18), Y(2)–O(21) 2.288(20), Y(2)–O(22) 2.305(19), Ba–O(8) 3.027(2), Ba–O(4) 2.874(18), Ba–O(5) 2.787(18), Ba–O(6) 2.822(18), Ba–O(7) 2.809(18), Ba–O(31) 2.646(22), Ba–O(32) 2.613(24). Selected bond angles (°) averaged: Y(1)–O–C(Et) 126.5(20), Y(2)–O–C(Et) 127.1(20), Ba–O–C(Et) 110.3(20).

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† *Synthesis*: All experiments were carried out under anhydrous conditions using standard vacuum-line and Schlenk techniques. After dissolution of Ba (1.98 g, 14.4 mmol) in a hot mixture of Pr^{i}OH–EtOH (35 ml : 5 ml) and filtration of the resulting solution, $Y_5O(OPr^i)_{13}$ (3.54 g, 2.88 mmol) in toluene (50 ml) was added and stirred at reflux temperature with dpmH (2.38 ml, 14.4 mmol) for 5 h. The concentration of the limpid orange solution and the addition of pyridine (1 ml) yielded, at room temp., single colourless parallelepiped crystals: yield 40%. The same product was obtained with a 1 : 2 (Y : Ba) molar ratio.

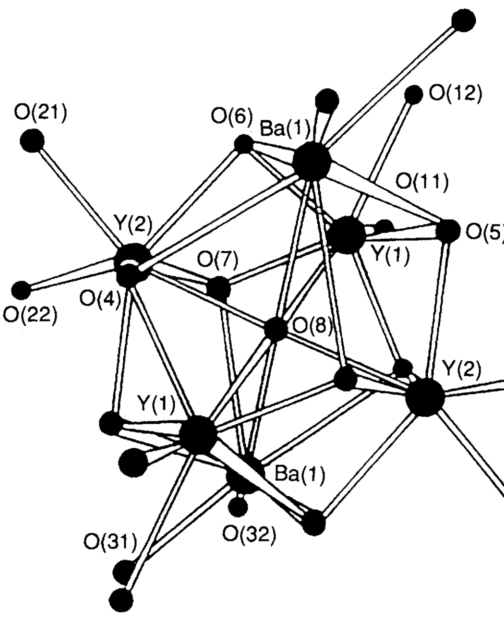
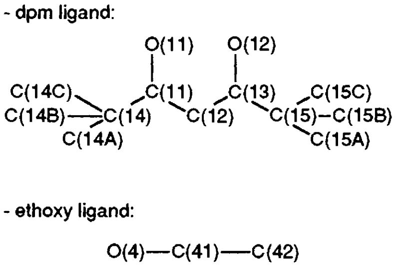


Fig. 2 Oxygen packing in the $Y_4Ba_2O_{21}$ core

chiometry (molar ratio 1 : 1 : 1 or 1 : 2 : 1 for Y : Ba : dpmH), single crystals of **1** were obtained at room temperature after concentration and addition of pyridine, as colourless parallelepipeds. Surprisingly, the pyridine, which is essential for obtaining suitable crystals for a X-ray analysis, acts neither as a ligand nor as a solvate. Moreover, the dry crystallized compound only displays ethoxy groups despite the high rate of isopropyl alcohol in the solution according to the elemental analysis and the ^1H NMR spectrum.‡ The latter reveals, at room temperature, a single environment for the CH_2 of the EtO groups whereas the CH of the dpm ligands present three resonances and the area of the methyl protons shows a complex signal. Low-temperature NMR studies show that the broad methyl resonances sharpen to one triplet for the Me of the OEt groups and to one unresolved multiplet for the Me of the dpm ligands whereas the other patterns are unchanged at 260 K; then, integration establishes eight OEt ligands for six dpm groups.§ The presence of only EtO groups can be mainly correlated with the steric factors of the alkyl groups; it is actually known that the facility for interchanging alkoxy groups increases from tertiary to secondary to primary groups. Mass losses, observed in the thermogravimetric analysis, agree with the presence of ethoxy ligands; three steps in the range of 100–200, 200–300 and 300–400 °C correspond to the eight EtOH, four dpmH and two dpmH removal, respectively. The heterometallic nature of **1** is suggested by the mass spectrometric analysis, as fragments containing both yttrium and barium atoms were identified at *m/z* 825, 727, 638, 581, 455 and 398; it was confirmed by an X-ray structure determination.¶ The molecule is centrosymmetric and lies on a crystallographic centre of symmetry, so that the asymmetric unit in the cell is only half of the molecule. This results in a μ_6-octachedral coordination for the oxygen O(8) located at the centre of the molecule (Fig. 2). The coordination angles around O(8) correspond to an almost perfect octahedral geometry (maximum angle deviation is 0.8°). This octahedron is slightly elongated with the Ba–O(8) distance [3.027(2) Å] longer than the Y–O(8) distances [2.363(3) and 2.378(3) Å]. The eight triangular faces of the octahedron are capped by a μ_3-OEt ligand. dpm ligands are only found in terminal positions and in addition to the oxo ligand give a coordination number of 7 for both Ba and Y atoms. The Ba–O and Y–O bond lengths are in good agreement with the literature.[7] A noteworthy point is that the Ba–O(Et) bond lengths are significantly longer than the Ba–O(dpm) ones whereas no significant differences are observed for the Y–O distances. Furthermore, the Ba–O–C(Et) angles (averaged to 110.3°) are smaller than the Y–O–C(Et) angles (126.8°) indicating that the π-donation from the OEt ligands is more important to Y than to Ba atoms. This is in agreement with the oxidation state of both metals (formally +2 for Ba and +3 for Y).



Atom labelling

In contrast to the reported structures of related barium and yttrium derivatives, which had square pyramidal $M_5(\mu_5\text{-}O)$ units,[7,8] we find here a fully encapsulated oxo ligand, as in $[H_4Ba_6(\mu_6\text{-}O)(OCH_2CH_2OMe)_{14}]$.[9] Among the bimetallic alkoxides with a $M_2M'_4$ stoichiometry, a similar structure—$M_2M'_4$ octahedron encapsulating a $\mu_6\text{-}O^{2-}$ unit—is adopted

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‡ Note: when the synthesis was performed in only EtOH, the resulting compound was different from complex **1**. Work on its crystal X-ray diffraction is in progress. Further work is in progress to elucidate the role of Pr^iOH.

§ *Selected spectroscopic data*: ^1H NMR (250 MHz, $CDCl_3$) 293 K: 0.90, 1.02, 1.06 (m, CH_3), 3.72 (q, CH_2), 5.42, 5.51, 5.59 (3s, CH); 260 K: 0.97, 1.08 (m, CH_3), 1.15 (t, CH_3), 3.70 (q, CH_2), 5.47, 5.55, 5.60 (3s, CH). IR (Nujol, ν/cm^{-1}): 1595–1581 ($\nu_s C{\cdots}O$), 1541 ($\nu_s C{\cdots}C$), 1247–1220 (νC–C), 796 (πC-H), 564, 515, 504, 469 (νM–OR). MS (EI, 70 eV, *m/z*): $Y_2Ba(dpm)_2(OEt)(Bu^tCOCH)$ (6%), $Y_2Ba(dpm)_2(OEt)$ (2%), $YBa(dpm)_2(OEt)$ (13%), $YBa(dpm)_2(OEt) - Bu^t$ (65%), YBa(dpm)(OEt) (100%), $YBa(dpm)(OEt) - Bu^t$ (12%), Ba(dpm) (24%), $Ba(Bu^tCOCHCO)$ (15%), Bu^tCO (11%), Bu^t (42%). Thermogravimetric analysis: (Ar, 300 °C h^{-1}, 50–900 °C) in the range 100–200 °C 16.5 wt. loss (8 HOEt); 200–300 °C 31.8% wt. loss (4 dpmH); 300–400 °C 15.9% wt. loss (2 dpmH). Found: C, 46.5; H, 7.6; Ba, 12.6; Y, 16.8. Calc. for $C_{82}H_{154}O_{21}Ba_2Y_4$: C, 46.7; H, 7.3; Ba, 13.0; Y, 16.9. Compound **1** is soluble and non-volatile.

¶ The single crystal chosen for the X-ray analysis is indeed representative of the bulk sample according to the X-ray powder pattern, which only shows diffraction peaks in agreement with those calculated from the single crystal unit cell. *Crystal data* for $C_{82}H_{154}O_{21}Ba_2Y_4$: $M = 2105$, crystal size 0.3 × 0.3 × 0.4 mm, triclinic, $a = 14.470(4)$, $b = 15.380(4)$, $c = 15.418(5)$ Å, $\alpha = 116.57(2)$, $\beta = 96.51(2)$, $\gamma = 101.99(2)°$, $U = 2916.3(14)$ Å^3, space group $P\bar{1}$, $Z = 1$, $F(000) = 1082$, $D_c = 1.199$ Mg m^{-3} μ(Mo-Kα) = 2.68 mm^{-1}; 5698 reflections collected with $4 \leqslant 2\theta \leqslant 40$ at 293 K; of these 5013 were unique and 3359 which had $F \geqslant 6\sigma(F)$ were used in structural analysis. The data were collected on a Siemens P3 diffractometer using Mo-Kα (λ = 0.71073 Å) radiation. Barium and yttrium atoms were found by analysis of a three-dimensional Patterson map using SHELXS 86.[13] All remaining non-hydrogen atoms were found by successive electron density map calculations using SHELX 76.[14] The structure was refined by least-squares techniques. Refinements converge to $R = 9.28\%$, $R_w = 12.01\%$ for 368 variables. These relatively high values for R and R_w can reasonably be attributed to the fast scan speed used for data collection (min = 9.77° min^{-1}; max = 14.65° min^{-1}). This affects the precision of the intensity measurements but was necessary in order to avoid any crystal decay problems due to X-ray exposure. In view of keeping the data : variables ratio close to 10 (9.1), only OEt ligands and atoms from the dpm ring were refined anisotropically. Anomalous dispersion terms were applied. All calculations were performed on a VAX 3100 computer. Atomic coordinates, bond lengths, angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

by $[Na_2Gd_4(\mu_6\text{-}O)(\mu_3\text{-}OBu^t)_8(OBu^t)_4]$,[10] $[Zr_2K_4(\mu_6\text{-}O)(\mu_3\text{-}OPr^i)_8(OPr^i)_2]$[11] and $[Zr_2Co_4(\mu_6\text{-}O)(\mu_2\text{-}OPr^i)_8(OPr^i)_2(acac)_4]$.[12] Although the mode of formation of the oxo group is not clear, its presence seems to be necessary in order for the structure to be stable.

We thank the CNRS PIRMAT for financial support.

Received, 13th April 1992; Com. 2/01938H

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