Alkoxides with Polydentate Alcohols: Synthesis and Structure of $[Y(OC_2H_4OMe)_3]_{10}$, a Hydrocarbon Soluble Cyclic Decamer

Olivier Poncelet,[a] Liliane G. Hubert-Pfalzgraf,*[a] Jean-Claude Daran,[b] and R. Astier[c]

[a] *Laboratoire de Chimie Moléculaire, Unité de Recherche Associée au CNRS, Université de Nice, Parc Valrose, 06034 Nice, France*

[b] *Laboratoire de Chimie des Métaux de Transition, Unité de Recherche Associée au CNRS, 4 Place Jussieu, 75230 Paris Cédex 05, France*

[c] *Laboratoire de Physicochimie des Matériaux, Unité de Recherche Associée au CNRS, Université de Montpellier II, 2 Place Eugène Bataillon, 34060 Montpellier Cédex, France*

Compound $[Y(OC_2H_4OMe)_3]_{10}$ was obtained either by direct attack on yttrium turnings by 2-methoxyethanol in toluene or by alcoholysis of $Y_5O(OPr^i)_{13}$; its *X*-ray structure analysis reveals a centrosymmetric cyclic arrangement of 10 yttrium atoms, each of these being hepta-co-ordinated.

The alkoxide chemistry of transition metals and lanthanides consists mainly of derivatives of classical primary, secondary, or tertiary alcohols.[1] Data concerning derivatives with potential polydentate alcohols such as alkoxyalcohols or alkanolamines, for instance, are scarce, although these derivatives are used as additives in sol-gel techniques in order to avoid formation of heterogeneous media, to slow down hydrolysis rates and/or stabilize gels.[2]

2-Methoxyethanol has been more extensively used to obtain $YBa_2Cu_3O_{7-x}$ *via* sol-gel techniques.[3] An yttrium derivative, tris(2-methoxyethanolate)yttrium has been mentioned by several groups. Synthesis routes such as anodic dissolution of the metal, and the reaction between yttrium trichloride and the appropriate alkali alkoxide[4] have been used, but characterization has been limited to microanalyses. Obtention of this product by dissolution of yttrium acetate in the alcohol has also been claimed.[3]

We report here the preparation of $[Y(OC_2H_4OMe)_3]_{10}$, either by direct attack of the metal or by solvolysis of an yttrium oxoalkoxide, and its *X*-ray crystal structure (Figure 1). Although some transition metal methoxyethanolates have been obtained by cleavage of the carbon–oxygen of 1,2-dimethoxyethane,[5] structural data are, to our knowledge, limited to those of $[Mg_4(OC_2H_4OMe)_6]^{2+}$.[6]

$[Y(OC_2H_4OMe)_3]_{10}$† has been obtained in nearly quantitative yield, independently of the synthetic route used; direct attack on Y turnings or alcoholysis of $Y_5O(O\text{–}Pr^i)_{13}$[7] at room temperature. The compound is highly soluble (monocrystals have been grown in ligroine), air-sensitive, and non-volatile. NMR spectra (^1H and $^{13}C\{^1H\}$) show several types of alkoxo groups but peak overlapping leads to quite complex and poorly informative spectra. The structure was elucidated by *X*-ray spectroscopy.‡

The molecular structure consists of a discrete centrosymmetric cyclic arrangement of 10 yttrium atoms (Figure 1), the metal being hepta-co-ordinated. All yttrium atoms have a similar environment which may be regarded as a pentagonal bipyramid. The co-ordination polyhedron of oxygen atoms on

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† *Selected spectroscopic data* for $Y_{10}(OC_2H_4OMe)_{30}$: IR (mineral oil) (Y–OR) 575, 530, 430 cm^{-1}. Satisfactory elemental analysis (C, H) was obtained.

‡ *Crystal data* for $C_{45}H_{105}O_{30}Y_5$: $M = 1544$, monoclinic, space group $P2_1/c$, $a = 13.640(6)$, $b = 20.331(8)$, $c = 24.804(9)$ Å, $\beta = 95.45(3)°$, $U = 6841$ Å^3, $D_c = 1.499$ g cm^{-3} for $Z = 4$, μ (Mo-K_α) = 42.94 cm^{-1}; 5339 data were collected at low temperature (−160 °C) on a Nonius CAD-4 diffractometer using graphite monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å). Yttrium atoms were found using SHELXS.[8] All remaining non-hydrogen atoms were located on successive difference electron density maps. The structure was refined by least-squares techniques with approximation (in three blocks) to the normal matrix using CRYSTALS.[9] 1845 reflections with $I > 2\sigma(I)$ were used to solve and refine the structure: $R = 0.0569$, $R_w = 0.0635$, 346 variables. In view of the low ratio variables/data = 5.3, only Y atoms were refined anisotropically. Of the five terminal monodentate alkoxo groups, two are disordered. These disorders which affect the C–O–Me ether groups, have not yet been completely sorted out. Anomalous dispersion terms were applied. Empirical absorption corrections using DIFABS[10] were made. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

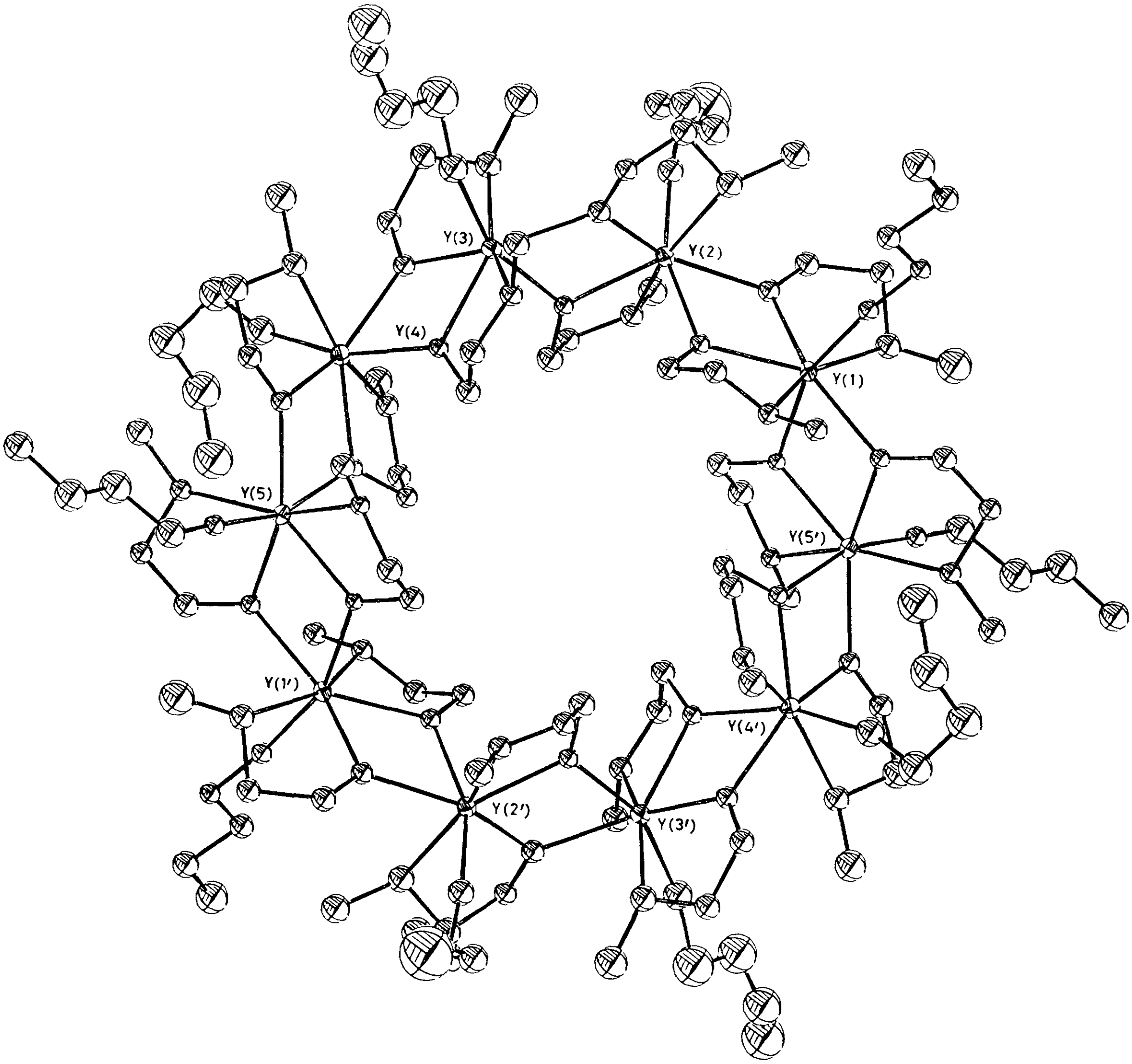

Figure 1. ORTEP view of the molecular structure of $[Y(OC_2H_4OMe)_3]_{10}$.

each metal results from one terminal monodentate alkoxo group, two chelating 2-methoxyethoxo groups, the alkoxo moieties of which are bridging to another Y atom while the alkoxide oxygen atoms of two other chelating 2-methoxyethoxo groups borne by a third yttrium atom are also bonded to the first yttrium (Figure 2). Each yttrium atom is thus linked to two other yttrium atoms through the alkoxo functionality of the methoxyethoxo groups. This arrangement of five yttrium atoms is quite regular (distances of 3.77 to 3.79 Å between two adjacent metals) and their equivalent positions, related by an inversion centre, give the ring of Figure 1. The size of the cavity as indicated by the contacts between carbon atoms is about 7 Å.

The Y–O bond distances uniformly follow the pattern Y–O (ether) > Y–O (bridging alkoxo) > Y–O (terminal alkoxo) and range from 2.07 to 2.57 Å. The Y–O bridge distances are nearly similar. The Y–O bond lengths involving the alkoxide functionality, terminal or bridging, are significantly shorter than the sum of the covalent radii (2.35 Å). Angles Y–O–C to terminal alkoxide ligands are nearly linear (162—177°) and account for the short Y–O bond lengths (average 2.09 Å). However, these values are larger than those obtained for other terminal alkoxo groups linked to yttrium, although the Y–O–C angles are comparable. The Y–O co-ordination bonds involving the ether functionality (average 2.52 Å) are longer than the values generally observed for Y–O(THF) bonds (THF = tetrahydrofuran) (2.33—2.45 Å).[11] Yttrium, like lanthanides, can commonly accommodate a high co-ordination number such as eight; however hexa-co-ordination, as also observed for the oxide Y_2O_3, seems to be favoured for yttrium(III) alkoxides. Thus $[Y(OC_2H_4OMe)_3]_{10}$ represents the first example of an yttrium or lanthanide alkoxide in which the metal is hepta-co-ordinated. The increase in co-ordination number may account for the lengthening of some Y–O bonds as a way to reduce steric crowding around the metal.

2-Methoxyethanol appears to be a very reactive alcohol, as evidenced by the solvolysis of the yttrium–oxo bond of $Y_5O(O\text{-}Pr^i)_{13}$ and alcoholysis at room temperature, the fast attack of the metal (by comparison with propan-2-ol) and the dissolution of various insoluble yttrium species. This polydentate alcohol also allows stabilisation of an alkoxide with respect to an oxoalkoxide.[7]

The $[Y(OC_2H_4OMe)_3]_{10}$ decamer is so far the highest oligomer structurally characterized for homoleptic alkoxides {a cyclic arrangement also has been reported recently for $[ZrCl_2(O\text{-}Pr^n)_2]_6$}.[12] The remarkable solubility of this

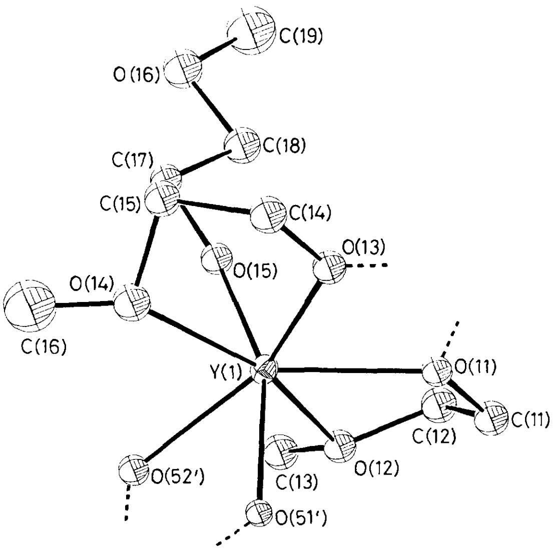

Figure 2. ORTEP view showing the environment around each yttrium atom. Selected bond lengths (Å) and angles(°) (average): Y–O terminal 2.09(2), Y–O (alkoxide functionality) in bridging position 2.29(2), Y–O (ether) 2.52(2); Y–O–C (terminal alkoxo group) 167.4(0).

decamer is probably due to its cyclic structure. Despite the hepta-co-ordination of the metal and the bidentate nature of most alkoxo groups, these remain labile, and further studies of the reactivity of $[Y(OC_2H_4OMe)_3]_{10}$ are in progress.

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