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COMMUNICATION

WATER ADDUCTS OF ARYLOXIDES: SYNTHESIS AND MOLECULAR STRUCTURE OF $Pr[OC_6H_2(CH_2NMe_2)_3\text{-}2,4,6]_3(H_2O)_2$

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Abstract—The alcoholysis of $Pr[N(SiMe_3)_2]_3$ by three equivalents of 2,4,6-$(Me_2NCH_2)_3C_6H_2OH$ [2,4,6-tris(dimethylaminomethyl)phenol = tamp-OH] in hexane gave Pr(O-tamp)$_3(H_2O)_2$ which has been characterized by X-ray crystallography. It represents the first example of a praseodymium aryloxide derivative. The complex displays two types of O-tamp ligands, one monodentate, two bidentate, leading to a seven-coordinated praseodymium in a distorted pentagonal bipyramidal configuration. The adduct is stabilized by intermolecular and intramolecular hydrogen bonds between the water molecules and the dangling amino groups.

Praseodymium oxides are involved in various materials such as in varistors[1] or in $PrBa_2Cu_3O_{7-y}$, an isolating material which might be associated to the high Tc superconductors in order to form heterostructures.[2] Chemical routes to such materials depend on the availability of suitable molecules to be converted into oxides in mild conditions, either in solution (sol–gel process) or in the vapor phase (Metal–Organic Vapor Phase Deposition, MOCVD).[3] The molecular chemistry of praseodymium remains scarce.[4] Our investigations on praseodymium alkoxides have shown that they are prone to form polynuclear oxo-aggregates which display limited solubility and/or volatility. This is particularly favored by the long work-up from the direct reaction between metal chips and alcohols. With alcohols such as isopropanol or 2-methoxyethanol, clusters such as $Pr_5O(OiPr)_{13}$[5] and $[Pr_4O(\mu_3,\eta^2\text{-}OR)_2(\mu,\eta^2\text{-}OR)_4(\mu,\eta1\text{-}OR)(OR)(OPMe_3)]_2$[5] (R = C_2H_4OMe) have been obtained respectively. A variety of monomeric or dimeric lanthanide aryloxides (Ln = Y, La, Ce, Yb) based on substituted phenols has been described.[4] Bulky phenols having Lewis base sites were envisioned as a means to achieve saturation of the praseodymium coordinate sphere in monomeric and/or oligomeric species of low nuclearity. Such ligands have previously been used to control the aggregation of barium and calcium derivatives.[6] The 2,4,6-tris(dimethylaminomethyl)phenoxide which is potentially a tetradentate ligand, has for instance been shown to act as a bridging, tridentate ligand in $Ba_4(\mu_4\text{-}O)[2,4,6\text{-}(Me_2NCH_2)_3C_6H_2O]_6$.

Alcoholysis of $Pr[N(SiMe_3)_2]_3$ by three equi-

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valents of 2,4,6-$(Me_2NCH_2)_3C_6H_2OH$ [2,4,6-tris (dimethylaminomethyl)phenol = tamp-OH] in hexane at room temperature led to the formation of a bright yellow solution and a yellowish precipitate (**1**), whose elemental analysis corresponds to $[Pr(O\text{-}tamp)_3]_n$ (yield = 59%).† After filtration and concentration, yellow crystals‡ of **2** were isolated in 23% yield. The paramagnetism of compound **2** precluded the acquisition of informative NMR spectra and its identity was thus established by single crystal X-ray diffraction.§

Compound **2** corresponds to a monomeric praseodymium(III) aryloxide adduct, $Pr(O\text{-}tamp)_3(H_2O)_2$, whose molecular structure is shown in Fig. 1. The O-tamp ligand displays two types of coordination modes, one monodentate and two bidentate, one *ortho*-dimethylaminomethyl group being linked to the metal. This ensures heptacoordination (five O-donors, two N-donors) for praseodymium, the stereochemistry of the metal corresponding to a distorted pentagonal bipyramid with bite angles of the bidentate O-tamp ligands of 71.4(1)° av. and thus comparable to these of β-diketonates. The main feature is the presence of the two water molecules which occupy *cis* positions [$\angle$O(4)—Pr—O(5) 75.9(1)°]. The Pr—O bond distances range from 2.269(3) to 2.508(3) Å. They are slightly shorter for the monodentate aryloxide ligand [Pr—O(3) 2.269(3) Å] than for the bidentate ones [Pr—O(1) 2.311(3), Pr—O(2) 2.280(3) Å] while the Pr—$O(H_2O)$ bonds are the longest ones [2.500(3) Å av.]. The Pr—O—C angles vary from 132.0(2) to 163.1(2)°, the more obtuse angle being associated with the monodentate aryloxide ligand. The Pr—N bond distances are longer [2.745(3) Å av.] than the Pr—O ones. The Pr—OR and Pr—N values fall in the range observed for the few structurally characterized praseodymium alkoxides such as $\{Pr[OCMe(CF_3)_2]_3\}_3$[7a] or $\{Pr[OCMe(CF_3)_2]_3(NH_3)_2\}_2$.[7b] The Pr—$O(H_2O)$ distances are comparable to these found for instance for $[Pr(OAc)_3(H_2O)_{1.5}]_m$, $m = 2$ or ∞.[8]

Short O···N distances between the two water molecules and the dangling amino groups suggest the presence of hydrogen bonds.[9] Each water molecule is actually involved in two hydrogen bonds. O(4) is involved in one intermolecular [O(4)—H···N(5) 2.810(5) Å] and one intramolecular interaction [O(4)—H···N(7) 2.772(5) Å] while O(5) interacts with dangling amino groups of the same molecule [O(5)—H···N(9) 2.848(5), O(5)—H···N(3) 2.794(5) Å]. The presence of hydrogen-bonding in the solid state is also confirmed by the broad ν(OH) absorption in the IR at 3126 cm^{-1}.

The formation of **2** is reproducible and the origin of the water molecules is probably due to the highly hygroscopic aminoalcohol (Aldrich) used. Compound **1** is poorly soluble in aliphatic hydrocarbons, but more soluble in toluene, thus suggesting limited oligomerization. Surprisingly, no stable adduct was formed with tetrahydrofuran (THF). By contrast, water appears as a favorable ligand for the oxophilic praseodymium center. Indeed, **2** is easily formed by controlled addition of water to **1** in toluene or by exposure of **1** to air for 2 h as evidenced by the appearance in the IR spectrum of a ν(OH) stretching absorption band at 3126 cm^{-1} and by the modification of the Pr—O absorption bands. These results indicate that aryloxides with potential donors sites are, like fluoroalkoxides,[10] able to form stable complexes with water as a ligand and are thus less likely to be hydrolyzed than the classical metal alkoxides which are rapidly converted into oxo or hydroxo deriva-

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† *Spectroscopic data of* **1**: IR (cm^{-1}): 1610, 1560 ν(C=C); 1286, 1261, 1173, 1144, 1097, 1037, 1001, 990, 944, 889, 836, 815, 643; 559, 514, 360 ν(Pr—O). Found: C, 57.5; H, 8.9; N, 13.1. Calc. for $C_{45}H_{78}O_3N_9Pr$: C, 57.9; H, 8.4; N, 13.5.

‡ *Spectroscopic data of* **2**: IR (cm^{-1}): 3126 ν(OH); 1610, 1564 ν(C=C); 1263, 1247, 1176, 1146, 1100, 1038, 1029, 1001, 990, 943, 892, 887, 834, 815, 643; 561, 517, 421, 381 ν(Pr—O). ESR (toluene, 20°C): $\langle g \rangle$ = 2.240.

§ *Crystal data of* **2**: $C_{45}H_{82}O_5N_9Pr$, $M = 969$, a = 16.917(4), b = 16.847(2), c = 19.514(3) Å, β = 105.28(2), V = 5365(22) $Å^3$, $Z = 4$, monoclinic, $P2_1/n$, $\mu = 9.49$ cm^{-1}. Crystals of **2** suitable for X-ray were grown by adding toluene to the filtrate and cooling at 10°C. Data were collected on an Enraf–Nonius CAD4 diffractometer with graphite monochromated Mo-K_α radiation (λ = 0.71069 Å) in the θ-2θ mode. Corrections were made for Lorentz, polarization and absorption effects. Computations were performed using CRYSTALS[11] adapted on a Microvax-II computer. Scattering factors and corrections for anomalous dispersion were taken from.[12] Solution of the structure was accomplished by using standard Patterson–Fourier techniques ($R = 0.038$, $Rw = 0.047$) from 7965 unique observed reflections ($I > 3\sigma(I)$) with $4 < 2\theta < 56°$, measured at room temperature with Mo-K_α radiation (λ = 0.71070 Å). All non-hydrogen atoms were anisotropically refined. Hydrogen atoms were located on a difference Fourier map; their coordinates were refined with an overall refinable isotropic thermal parameter. Disorder of the non-coordinated NMe_2 groups of the phenol, C(12)—N(2)—C(11), C(29)—N(6)—C(30) and C(41)—N(8)—C(42) was observed but it was not modeled.

Atomic coordinates, non-essential bond lengths and angles, and thermal parameters have been deposited with the Cambridge Crystallographic Data Center.

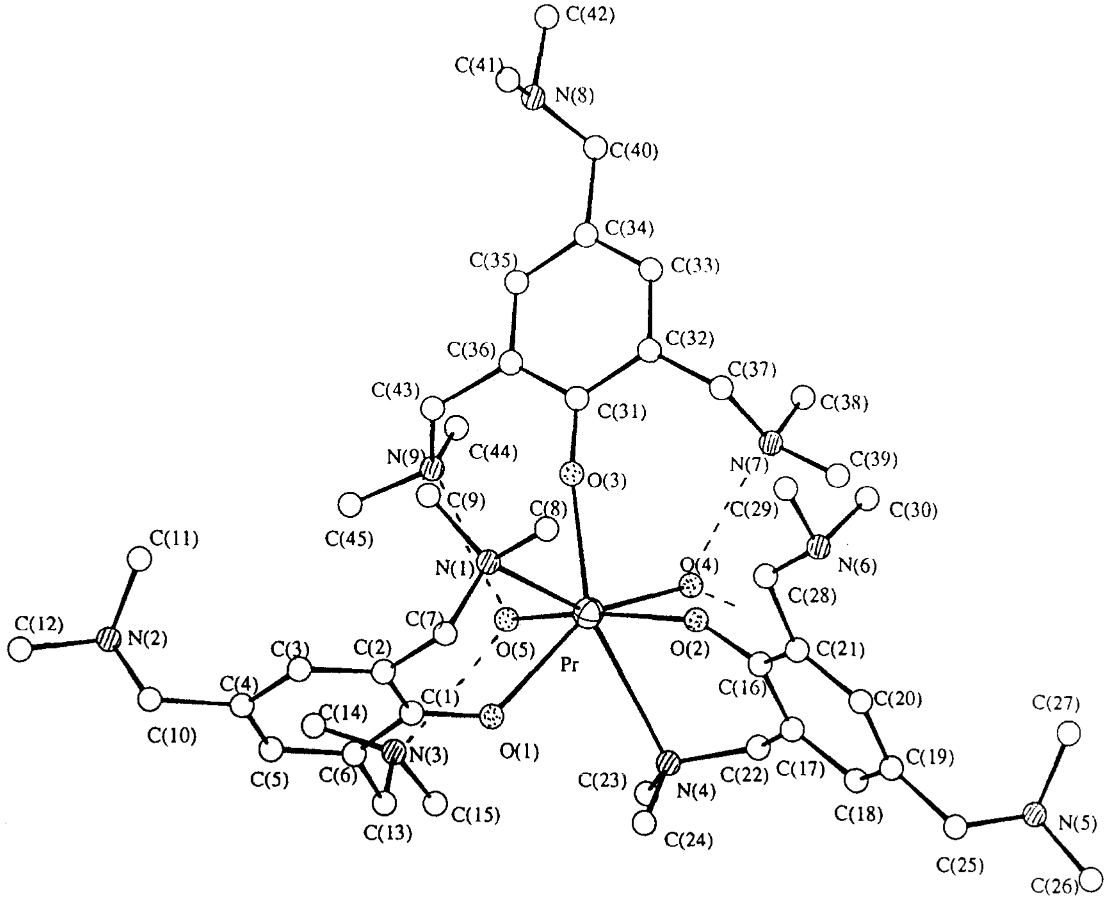

Fig. 1. Molecular structure of $\mathrm{Pr(O\text{-}tamp)_3(H_2O)_2}$ showing the atom labeling scheme. Dotted lines indicate hydrogen bonds. Selected bond lengths (Å): Pr—O(1) 2.311(3); Pr—O(2) 2.280(3); Pr—O(3) 2.269(3); Pr—O(4) 2.491(3); Pr—O(5) 2.508(3); Pr—N(1) 2.760(3); Pr—N(4) 2.729(3); O(4)—H ··· N(5) 2.810(5); O(4)—H ··· N(7) 2.772(5); O(5)—H ··· N(9) 2.848(5); O(5)—H ··· N(3) 2.794(5). Bond angles (°): O(1)—Pr—O(2) 113.7(1); O(1)—Pr—O(3) 130.5(1); O(1)—Pr—O(4) 133.5(1); O(1)—Pr—O(5) 74.2(1); O(2)—Pr—O(3) 104.0(1); O(2)—Pr—O(4) 86.8(1); O(2)—Pr—O(5) 160.7(1); O(3)—Pr—O(4) 77.3(1); O(3)—Pr—O(5) 80.7(1); O(4)—Pr—O(5) 75.9(1); O(1)—Pr—N(1) 72.7(1); O(1)—Pr—N(4) 73.3(1); O(2)—Pr—N(1) 89.6(1); O(2)—Pr—N(4) 70.0(1); O(3)—Pr—N(1) 76.8(1); O(3)—Pr—N(4) 152.9(1); O(4)—Pr—N(1) 152.2(1); O(4)—Pr—N(4) 76.0(1); O(5)—Pr—N(1) 109.7(1); O(5)—Pr—N(4) 97.1(1); N(1)—Pr—N(4) 128.2(1); Pr—O(1)—C(1) 132.0(2); Pr—O(2)—C(16) 146.2(3); Pr—O(3)—C(31) 163.1(2).

tives.[3] Compound **2** can formally be considered as the first step in the hydrolysis of $\mathrm{[Pr(O\text{-}tamp)_3]_m}$.

$\mathrm{Pr[OC_6H_2(CH_2NMe_2)_3\text{-}2,4,6]_3(H_2O)_2}$ and its precursor $\mathrm{[Pr(O\text{-}tamp)_3]_m}$ represents the first praseodymium aryloxides reported. Compound **2** has various potential reactive sites, namely the two H_2O molecules as well as the dangling amino groups, for building up heterometallic aggregates and investigation of its reactivity is in progress.

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