Synthesis, Reactivity and X-Ray Crystallographic Characterization of Chloro(propan-2-ol)bis(tetraisopropoxoaluminato)praseodymium(III) Dimer, $[\{Pr[Al(OPr^i)_4]_2(Pr^iOH)(\mu\text{-}Cl)\}_2]$

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The product of the 1 : 2 reaction between $PrCl_3 \cdot 3Pr^iOH$ and $K[Al(OPr^i)_4]$ in benzene–propan-2-ol, has been shown by X-ray crystallographic analysis to be a heptacoordinated heteroleptic alkoxometallatopraseodymium(III) complex **1**, which affords solvated and unsolvated species respectively by ligand displacement reactions and distillation *in vacuo*.

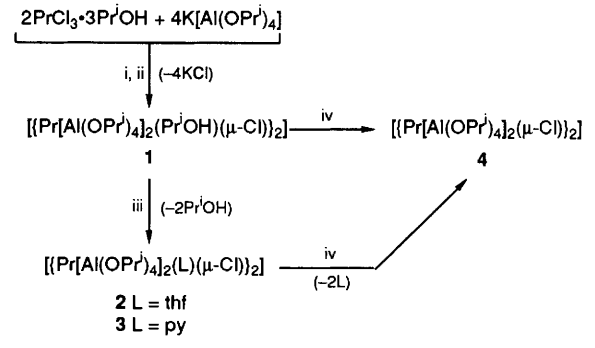
There is a growing interest[1,2] in the chemistry of chloro(alkoxo)metallate derivatives, particularly as synthons for a variety of novel stable heteropolymetal alkoxide species,[3–5] which have been shown to yield ultrahomogeneous ceramic materials by the sol–gel technique.[6,7]

As part of extensive studies on heterometal lanthanoid alkoxides,[8,9] we report the preparation, reactions (Scheme 1) and characterization, including X-ray structure of $[\{Pr[Al(OPr^i)_4]_2(Pr^iOH)(\mu\text{-}Cl)\}_2]$ (Fig. 1).

Derivatives† **1**, **2**, **3** and **4** were synthesized as shown in Scheme 1. Single crystals of $[\{Pr[Al(OPr^i)_4]_2(Pr^iOH)(\mu\text{-}Cl)\}_2]$ were obtained from CH_2Cl_2–C_6H_{14} at −20 °C as pale-yellow prisms.‡

Complex **1** is a centrosymmetric dimer composed of two triangular $Al_2Pr(\mu\text{-}OPr^i)_4(OPr^i)_4(Pr^iOH)^+$ units linked by two chloride bridges, praseodymium being heptacoordinated. It may be relevant to mention a chloride bridging reported in the complex, $[\{Al_3Nd_6(\mu_2\text{-}Cl)_6(\mu_3\text{-}Cl)_6(\mu_2\text{-}Et)_9Et_5(OPr^i)\}_2]$[10] as well as $[\{Cd[Zr_2(OPr^i)_9](\mu\text{-}Cl)\}_2]$.[2] The coordination polyhedron formed by five oxygens [from two chelating $Al(OPr^i)_4^-$ groups and one propan-2-ol molecule] and two bridging chlorine atoms around a praseodymium atom may preferably be envisaged as a distorted capped trigonal prism(C_{2v}). However, when viewed in a different perspective,[11,12] the possibility as a distorted capped octahedron (C_{3v}) or pentagonal bipyramid (D_{5h}) cannot be ruled out. The average Pr–O (chelate) distance 2.397 Å, lies midway between the observed 2.356 Å for heptacoordinated $[Pr(dpm)_3(tppo)]$[13] and 2.43 Å for $[\{Pr(dpm)_3\}_2]$, where dpm is dipivaloyl methane and tppo is triphenylphosphine oxide.[14] The Pr–O (propan-2-ol) distance is 2.525(8) Å.

The observed average Al–O bond distance in **1** is 1.724 Å,



Scheme 1 *Reagents and conditions*: i, C_6H_6–Pr^iOH, 60 °C, 12 h, followed by removal of volatiles *in vacuo* at room temp.; ii, crystallization (CH_2Cl_2–C_6H_{14}, −20 °C); iii, thf (tetrahydrofuran) or py (pyridine) (L), 30 °C, 12 h, followed by removal of volatiles *in vacuo* at room temp.; iv, distillation at *ca.* 200 °C/10^{-2} Torr

† Confirmed by satisfactory analytical (Pr, Al, Cl, OPr^i) results; ^1H and ^{13}C NMR spectroscopy and elemental data.

‡ *Crystal data*: $C_{54}H_{128}Al_4Cl_2O_{18}Pr_2$, crystal size 0.32 × 0.40 × 0.60 mm, monoclinic, space group *C2/c*, M = 1526.2, a = 25.181(6), b = 16.937(3), c = 19.376(3) Å, β = 91.60(2)°, U = 8260(3) Å^3, Z = 4 dimer, D_c = 1.227 mg m^{-3}, μ(Mo-Kα) = 0.71073 Å, 7792 reflections collected with $3.5 < 2\theta < 50°$ at 295 K; of these 7299 were unique and 4251 which had $F > 6.0\sigma(F)$ were used in structural analysis. The data were collected on a Siemens R3m/V Nicolet P3 diffractometer. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically, while hydrogen atoms (riding model) were given fixed isotropic thermal parameters. Refinement was carried out by use of the full-matrix least-squares method, using the Siemens SHELXTL PLUS(VMS) program system, giving R and R_w values of 0.0545 and 0.076, respectively. The atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

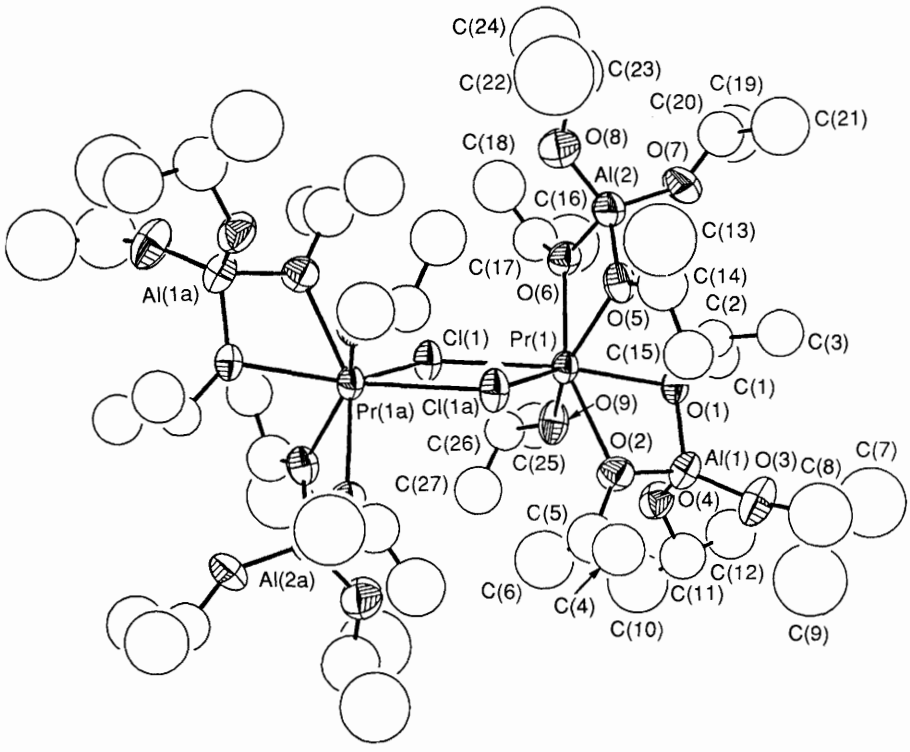


Fig. 1 Crystal structure of **1**, showing the atomic numbering. Important geometric parameters include: bond lengths (Å): Pr–Cl (average) 2.849(2), Pr-O (chelate) 2.397 (average), Al–O (average) 1.724; bond angles (°): Cl(1)–Pr(1)–Cl(1A) 72.3(1), Cl(1)–Pr(1)–O(6) 83.8(2), O(6)–Pr(1)–O(5) 62.7(2), O(6)–Pr(1)–O(1) 91.5(2), O(5)–Pr(1)–O(2) 110.1(2), O(9)–Pr(1)–O(2) 77.1(2), O(1)–Pr(1)–O(9) 72.9(2).

which may be compared with an average distance of 1.76 Å in $[\{Al(OPr^i)_3\}_4]$[15,16] and of 1.758 Å in $[\{Al(OBu^t)_3\}_2]$.[17]

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