

Nd[Al(*i*PrO)₄]₃, a novel tetranuclear alkoxide forming merohedrally twinned crystals

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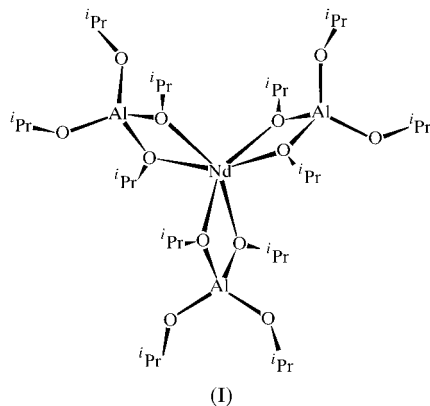
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The new tetranuclear alkoxide hexa- μ_2 -isopropoxy-1:2 κ^4 O;1:3 κ^4 O;1:4 κ^4 O-hexaisopropoxy-2 κ^2 O,3 κ^2 O,4 κ^2 O-trialuminium(III)neodymium(III), [Nd{Al(C₃H₇O)₄]₃, has a metal-oxygen NdAl₃O₁₂ core which consists of four metal atoms arranged in an approximately planar triangular geometry. The central Nd atom is six-coordinated by O atoms and the Al atoms are four-coordinated by O atoms.

Comment

Lanthanide-aluminium-based alkoxides have recently received much interest because of their structures in the solid state (Kritikos *et al.*, 2001). Another appealing feature of these compounds is that they can be used as precursors in oxide-based materials. Of particular interest is the potential use of [M{Al(*i*PrO)₄]₃ (M is Er, Eu or Nd) in high-purity optical materials (Westin *et al.*, 1998, 2000). We present here the structure of the title compound, (I), a new member of this series of materials.



As expected from its composition, compound (I) is almost isostructural with the orthorhombic [Er{Al(*i*PrO)₄]₃ (space group $P2_12_12_1$; Wijk *et al.*, 1996) and can be considered as a monoclinic deviation from the latter. There is no significant

difference in the molecular geometry of the two. The Er-phase, in contrast with the Nd-phase, was studied at room temperature, which might explain the difference in their space groups. It was found by means of *PLATON* (Spek, 1990) that (I) also possesses, though rather approximately, $P2_12_12_1$ symmetry with a maximum deviation of 0.9 Å. An additional pseudo- 2_1 axis relates two independent molecules of (I) present in the asymmetric unit, which thus have nearly identical geometry.

The point-group symmetry of the metal-oxygen core of (I) is close to C_3 , as determined by *SYMMOL* (Pilati & Forni, 2000); the r.m.s. deviation is estimated at 0.12 Å. The three Al atoms form a triangle, with the Nd atom in the centre. Nd and Al are interconnected by two bridging μ_2 -O atoms, with μ_2 -O–Nd– μ_2 -O angles close to 64.2 (2)°. Each Al has two additional isopropoxy O atoms completing the distorted tetrahedral coordination sphere. Al– μ_2 -O distances are close to the average value of 1.79 (1) Å, while terminal O atoms are located approximately 1.70 (1) Å from Al. The μ_2 -O–Al– μ_2 -O and O–Al–O valence angles are close to 89 and 118°, respectively. In addition, all six Nd–O bonds are close to the average value of 2.352 (11) Å. The coordination polyhedron of the Nd atom can be described as halfway between octahedral and trigonal prismatic, *i.e.* the triangular face of the octahedron is rotated around the threefold axis by 28°.

Interestingly, a solvated analogue, [Nd{Al(*i*PrO)₄]₃·*i*PrOH, of (I) has recently been reported by Veith *et al.* (2000). In this molecule, the central Nd atom is bonded to an additional protonated isopropoxy group and is thus seven-coordinated by O atoms. Accordingly, this leads to distortion of the molecule from C_3 symmetry to C_1 and an increase of the average Nd–O distance to 2.44 (6) Å. However, the NdAl₃ metal core still has planar geometry (point group C_3 , r.m.s. deviation 0.15 Å). The AlO₄ tetrahedra are similar to those in (I): the Al– μ_2 -O and Al–O bond distances are close to 1.8 and

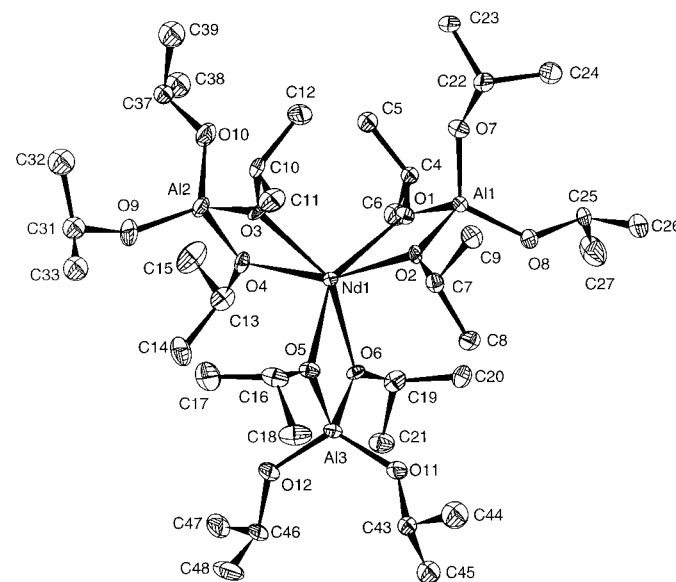


Figure 1

The molecular structure of (I), showing 30% probability displacement ellipsoids. H atoms have been omitted for clarity. Only the higher occupancy part of each disordered –CH(CH₃)₂ group and only one molecule from the asymmetric unit are shown.

1.7 Å, respectively, and the μ_2 -O—Al— μ_2 -O and O—Al—O valence angles are around 89 and 116°, respectively. These tetrahedra are somewhat different in the similar molecule [Al{Al(*i*PrO)₄}]₃ (Turova *et al.*, 1979; Folting *et al.*, 1991); while distances remain the same, angles change to 83° for μ_2 -O—Al— μ_2 -O and 120° for O—Al—O. It has been observed that [Nd{Al(*i*PrO)₄}]₃·*i*PrOH decomposes into [Nd{Al(*i*PrO)₄}]₃ during distillation under vacuum (Veith *et al.*, 2000).

Experimental

All reactions were performed under an argon atmosphere (<1 p.p.m. H₂O, O₂) in a glove-box. The toluene, 2-propanol (*i*PrOH) and *n*-hexane solvents were dried by distillation over CaH₂ under an inert atmosphere. The potassium and anhydrous NdCl₃ (Strem Chemicals, 99.9%) were used as purchased, while the Al₄(*i*PrO)₁₂ (Sigma, 99.9%) was recrystallized from toluene–*i*PrOH before use. Potassium (21.07 mmol) was dissolved in *i*PrOH–toluene (20 ml; 1:1, *v/v*) and Al₄(*i*PrO)₁₂ (21.08 mmol) was added with stirring. After 30 min, NdCl₃ (7.025 mmol) was added and 48 h later the mixture was centrifuged to precipitate the solid KCl formed in the reaction. The blue solution was evaporated to dryness and dissolved in toluene–*n*-hexane (1:1, *v/v*) and once again evaporated to dryness. Compound (I) was then crystallized over a period of more than one month from a concentrated *n*-hexane solution. FT–IR (nujol, cm^{−1}): 1184, 1171, 1138, 1126, 1119, 1033, 955, 862, 855, 830, 702, 673, 607, 568, 477, 448, 398. The peaks at 1200–1100 cm^{−1} correspond to C–C vibrations of the isopropyl groups.

Crystal data

[Nd{Al(C₃H₇O)₄}]₃
M_r = 934.21
 Monoclinic, *P*₂₁
a = 13.1476 (15) Å
b = 22.6558 (16) Å
c = 16.9355 (19) Å
 β = 90.221 (14)°
V = 5044.5 (9) Å³
Z = 4

D_x = 1.230 Mg m^{−3}
 Mo *K* α radiation
 Cell parameters from 5000 reflections
 θ = 6–22.9°
 μ = 1.129 mm^{−1}
T = 110 (2) K
 Irregular, pale blue
 0.40 × 0.20 × 0.15 mm

Data collection

Stoe IPDS diffractometer
 φ oscillation scans
 Absorption correction: numerical
 [*X-SHAPE* (Stoe & Cie, 1996)
 and *X-RED* (Stoe & Cie, 1996)]
T_{min} = 0.661, *T_{max}* = 0.849
 26 970 measured reflections
 9421 independent reflections (plus
 6949 Friedel-related reflections)

15 077 reflections with *I* > 2 σ (*I*)
R_{int} = 0.035
 θ_{max} = 26.08°
h = −16 → 16
k = −27 → 27
l = −20 → 20
 50–200 standard reflections
 frequency: 5 min
 intensity decay: none

Refinement

Refinement on *F*²
R [*F*² > 2 σ (*F*²)] = 0.031
wR(*F*²) = 0.069
S = 1.034
 16 370 reflections
 922 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0351P)^2 + 0.0284P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.002$
 $\Delta\rho_{max} = 0.68 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{min} = -0.92 \text{ e } \text{Å}^{-3}$
 Absolute structure: Flack (1983)
 Flack parameter = −0.022 (9)

The absolute structure of (I) was chosen according to the Flack parameter (Flack, 1983), based on 6949 Friedel pairs. The −CH(CH₃)₂ groups connected to O1, O9, O10, O11, O13, O19, O21 and O23 were disordered over two sites, which were refined isotropically. A common occupancy factor was used for every atom within any given disordered group. The sum of the occupancy factors of two disor-

Table 1
 Selected geometric parameters (Å).

Nd1—O3	2.339 (4)	Nd2—O14	2.346 (4)
Nd1—O1	2.351 (4)	Nd2—O18	2.347 (4)
Nd1—O6	2.353 (4)	Nd2—O16	2.351 (4)
Nd1—O4	2.361 (4)	Nd2—O15	2.352 (4)
Nd1—O2	2.361 (4)	Nd2—O17	2.364 (4)
Nd1—O5	2.362 (4)	Nd2—O13	2.366 (4)
Al1—O7	1.678 (5)	Al4—O20	1.692 (5)
Al1—O8	1.704 (5)	Al4—O19	1.693 (5)
Al1—O1	1.791 (5)	Al4—O13	1.780 (5)
Al1—O2	1.795 (4)	Al4—O14	1.799 (4)
Al2—O9	1.689 (5)	Al5—O22	1.694 (5)
Al2—O10	1.692 (5)	Al5—O21	1.701 (5)
Al2—O4	1.756 (5)	Al5—O15	1.778 (4)
Al2—O3	1.803 (5)	Al5—O16	1.802 (4)
Al3—O12	1.699 (5)	Al6—O24	1.697 (5)
Al3—O11	1.703 (5)	Al6—O23	1.707 (6)
Al3—O5	1.787 (5)	Al6—O18	1.795 (5)
Al3—O6	1.795 (4)	Al6—O17	1.795 (5)

dered groups connected to the same O atom was constrained to 1.0. The final values of the occupancy factors corresponding to the above O atoms were 0.19 (2), 0.39 (2), 0.38 (2), 0.38 (2), 0.39 (2), 0.42 (2), 0.43 (5) and 0.36 (2), respectively. 1,2-C—C bonding distances were restrained to the expected value of 1.52 Å, and 1,3-C···C interatomic distances were restrained to 2.45 Å. All H atoms were placed in calculated positions, with isotropic displacement parameters 1.2 times the *U_{iso}* of their respective parent C atom. CH₃ (C—H = 0.98 Å) and CH (C—H = 1.00 Å) groups were constrained to idealized geometries, with H atoms riding. The crystal under investigation was twinned by pseudo-merohedry, with the twin law 100, 0 $\bar{1}$ 0, 00 $\bar{1}$. The twin fraction was refined to 0.3510 (6).

Data collection: *IPDS Software* (Stoe & Cie, 1996); cell refinement: *IPDS Software*; data reduction: *IPDS Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1432). Services for accessing these data are described at the back of the journal.

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