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$(Tb_{0.9},Er_{0.1})_4TiO(O^iPr)_{14}$, a Novel Pentanuclear Oxo–Alkoxide

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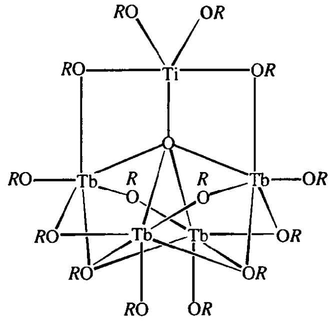
Abstract

The new pentanuclear alkoxide μ_5-oxo-bis(μ_3-isopropoxo)hexakis(μ_2-isopropoxo)hexakis(isopropoxo)tetraterbium(III)titanium μ_5-oxo-bis(μ_3-isopropoxo)hexakis(μ_2-isopropoxo)hexakis(isopropoxo)tetraerbium(III)-, titanium, with the composition $[(Tb_{0.9}Er_{0.1})_4Ti(\mu_5\text{-}O)(\mu_3\text{-}OR)_2(\mu_2\text{-}OR)_6(OR)_6]$ (R = ^{i}Pr = C_3H_7O) has a metal–oxygen Ln_4TiO_{14} core which consists of five metal atoms arranged in approximately trigonal-bipyramidal geometry, with a μ_5-O atom in the centre of the polyhedron. The lanthanide atoms are sixfold coordinated and the Ti atom is fivefold coordinated, both by O atoms.

Comment

Metal alkoxides are important precursors in the organic sol–gel process for obtaining various types of fine ceramics (Chandler, Roger & Hampden-Smith, 1993). When using alkoxides containing different metal ions in the same molecule, *i.e.* heterometallic alkoxides, extremely good homogeneity of the constituents can be obtained both in gels and final ceramics. The present study is part of a program involving rare-earth alkoxides that are to be used as precursors for optical materials, *e.g.* laser amplifiers and frequency up-conversion devices, as well as for anionic conductor ceramics. The optical rare-earth-doped materials may contain one or more rare-earth metals (Desurvire, 1991). The present paper reports an investigation of a precursor containing Tb and Er in the ratio 9:1, together with an optically 'silent' Ti atom. The title compound, (I), is isostructural with the bimetallic alkoxide $[(Sm)_4Ti(\mu_5\text{-}O)(\mu_3\text{-}OR)_2(\mu_2\text{-}OR)_6(OR)_6]$ (R = ^{i}Pr) (Daniele *et al.*, 1994) and has a molecular metal-atom framework similar to that of the homometallic alkoxide $[Nd_5(\mu_5\text{-}O)(\mu_3\text{-}OR)_2(\mu_2\text{-}OR)_6(OR)_5(HOR)_2]$ (R = ^{i}Pr) (Helgesson *et al.*, 1991).



(I)

The metal–oxygen framework of the novel termetallic alkoxide is formed by four hexacoordinated lanthanide atoms and a pentacoordinated Ti atom. The coordination sphere around the Ti atom constitutes a distorted trigonal bipyramid with two terminal O atoms, two μ_2-bridging O atoms and one μ_5-O atom. The angular distortions from ideal geometry are rather small. However, the two apical Ti—O bonds, involving μ_2-O atoms, are quite elongated compared with the equatorial Ti—O bonds involving terminal O atoms. These bond-length

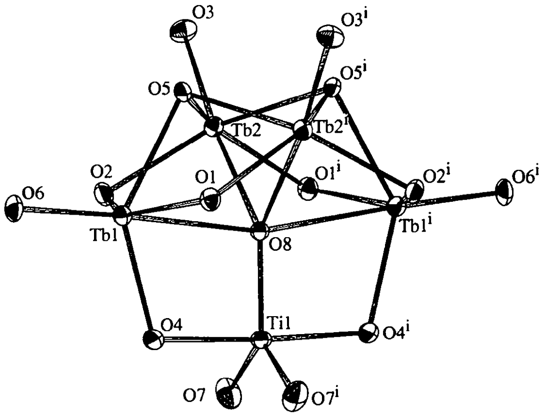


Fig. 1. The molecular structure showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity. [Symmetry code: (i) $1 - x, -y, z$.]

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differences between bonds to apical and equatorial O atoms are about 0.15 Å.

The (Tb,Er)—O bond lengths increase in the following order: terminal Ln—O*R* < Ln—μ_2-O*R* < Ln—μ_3-O*R* < Ln—μ_5-O. This bond-length variation of the different *M*—O bonding modes is in agreement with the general trend found for metal alkoxides (Hubert-Pfalzgraf, 1995; Mehrotra & Singh, 1996). The significant difference in bond length between Ln1—O8 and Ln2—O8 reflects the unequal distribution of the μ_2-O and μ_3-O binding modes on Ln1 and Ln2. Bond valence sum (BVS) calculations for trivalent Tb ions and the tetravalent Ti ion gave values of 3.18 and 4.21, respectively. Standard values of BVS parameters for oxides were used in the calculations (Brese & O'Keeffe, 1991). Weighting the BVS parameters, by the experimentally estimated Tb:Er ratio of 9:1, had minor effects on the BVS values.

The Ln—O—C bond angles of the two terminal isopropoxide groups are almost linear. This widening of the Ln—O—C angles together with the rather short Ln—O bond lengths could possibly be attributed to *sp* hybridization on O and a concomitant increase of the Tb—O bond order. Similar effects have been observed in other alkoxides that contain *f* elements, *e.g.* dinuclear uranium alkoxides and tetranuclear cerium isopropoxide (Cotton, Marler & Schwotzer, 1984; Yunlu *et al.*, 1991). This *M*—O—C bond-angle linearization effect is less pronounced at the Ti atom, where the terminal Ti—O—C bond angle is 152.6 (7)°.

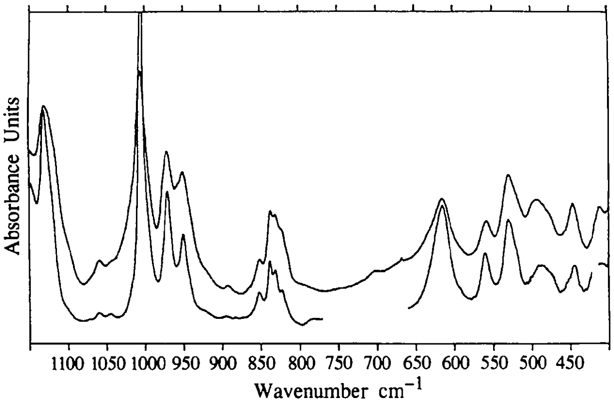

Fig. 2. FT-IR spectra of $(Tb_{0.9},Er_{0.1})_4TiO(O^iPr)_{14}$ as a solid in KBr (upper curve) and as a hexane solution. The plot of the solution (lower curve) spectrum has been removed where the solvent absorptions were strong.

Experimental

The synthesis was performed with precautions against oxygen and water contamination and the starting materials were all free of water. The experimental procedures are reported in detail elsewhere (Wijk *et al.*, 1996). $(Tb_{0.9},Er_{0.1})_4TiO(O^iPr)_{14}$ was prepared by dissolving 12.79 mmol of potassium in 2-propanol–toluene followed by addition of 1.066 mmol of $Ti(O^iPr)_4$. After 2 h, 3.836 mmol of $TbCl_3$ and 0.426 mmol of $ErCl_3$ were added and the mixture was reacted for 3 d at room temperature. The weakly pink-coloured solution was removed from the precipitated KCl and subsequent evaporation of the solution gave pale pink crystals of the title compound. The Tb/Er ratio was established by analysis on a scanning electron microscope (Jeol 820) equipped with an energy-dispersive spectrometer (Link 10000 AN). Infrared spectra of the alkoxide in the diagnostic C—O and *M*—O region 1250–400 cm^{-1} as a solid in KBr and as a hexane solution are shown in Fig. 2. The great similarity of the spectra shows that the molecular structure of the solid remains to a large extent in solution. The peaks of the solid-state spectrum are tentatively assigned as Ti—O and (Tb,Er)—O vibrations, 412, 446, 559, 617, 853, 893, 822, 831 and 837 cm^{-1}, with the C—O and C—C vibrations at 947, 971, 1005, 1042, 1069, 1101, 1119, 1129, 1149 and 1160 cm^{-1}.

Crystal data

[$Er_{0.4}Tb_{3.6}TiO(C_3H_7O)_{14}$]
$M_r = 1530.12$
Tetragonal
$I4_1cd$
$a = 21.4236\,(9)$ Å
$c = 25.757\,(3)$ Å
$V = 11821.8\,(17)$ Å^3
$Z = 8$
$D_x = 1.719$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 74 reflections
$\theta = 11.60–27.16°$
$\mu = 5.00$ mm^{-1}
$T = 170\,(2)$ K
Irregular
0.6 × 0.5 × 0.4 mm
Pale pink

Data collection

Stoe Stadi-4 diffractometer
$2\theta/\omega$ scans (width: 0.81–0.99° in ω)
Absorption correction: by integration
$T_{min} = 0.097$, $T_{max} = 0.158$
16 499 measured reflections
3607 independent reflections
2678 reflections with $I > 2\sigma(I)$

$R_{int} = 0.028$
$\theta_{max} = 27.5°$
$h = -1 \rightarrow 27$
$k = -1 \rightarrow 27$
$l = -1 \rightarrow 33$
4 standard reflections
frequency: 360 min
intensity decay: 9.2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.024$
$wR(F^2) = 0.063$
$S = 0.997$
3606 reflections
297 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.043P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = -0.006$
$\Delta\rho_{max} = 0.563$ e Å^{-3}
$\Delta\rho_{min} = -0.825$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute configuration: Flack (1983)
Flack parameter = 0.018 (13)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Tb1†	0.41506 (2)	0.08636 (2)	0.371432 (12)	0.03578 (8)
Tb2†	0.44011 (2)	−0.05904 (2)	0.426368 (14)	0.03443 (8)
Er1‡	0.41506 (2)	0.08636 (2)	0.371432 (12)	0.03578 (8)

Er2‡	0.44011 (2)	−0.05904 (2)	0.426368 (14)	0.03443 (8)
Ti1	1/2	0	0.28555 (6)	0.0378 (3)
O1	0.5086 (3)	0.1354 (3)	0.3826 (2)	0.0437 (14)
O2	0.3642 (3)	−0.0083 (3)	0.3834 (2)	0.0452 (14)
O3	0.3994 (3)	−0.1021 (3)	0.4896 (2)	0.0525 (12)
O4	0.4324 (3)	0.0657 (3)	0.2880 (2)	0.0443 (11)
O5	0.5464 (2)	−0.0468 (2)	0.4521 (2)	0.0366 (9)
O6	0.3482 (3)	0.1550 (3)	0.3786 (2)	0.0533 (12)
O7	0.4524 (3)	−0.0514 (3)	0.2482 (3)	0.076 (2)
O8	1/2	0	0.3580 (2)	0.0337 (12)
C1	0.5289 (5)	0.1969 (4)	0.3705 (5)	0.071 (3)
C2	0.3035 (7)	−0.0213 (8)	0.3754 (9)	0.125 (5)
C3	0.3757 (6)	−0.1389 (5)	0.5310 (4)	0.080 (3)
C4	0.4133 (4)	0.1000 (4)	0.2438 (3)	0.051 (2)
C5	0.5709 (4)	−0.0681 (4)	0.5012 (3)	0.048 (2)
C6	0.3021 (7)	0.2005 (6)	0.3829 (7)	0.113 (5)
C7	0.4009 (6)	−0.0645 (5)	0.2172 (5)	0.078 (4)
C8	0.4937 (6)	0.2435 (5)	0.3902 (6)	0.105 (5)
C9	0.5963 (5)	0.2076 (6)	0.3881 (6)	0.089 (4)
C10	0.2801 (9)	−0.0795 (8)	0.3861 (10)	0.198 (10)
C11	0.2621 (7)	0.0168 (8)	0.3621 (8)	0.178 (8)
C12	0.3914 (6)	−0.1095 (6)	0.5804 (4)	0.082 (3)
C13	0.3056 (7)	−0.1499 (7)	0.5220 (6)	0.124 (6)
C14	0.3422 (4)	0.1041 (5)	0.2416 (4)	0.070 (3)
C15	0.4415 (5)	0.1649 (5)	0.2469 (6)	0.091 (4)
C16	0.5575 (5)	−0.1390 (5)	0.5085 (5)	0.086 (4)
C17	0.6400 (5)	−0.0570 (4)	0.5061 (4)	0.064 (3)
C18	0.3094 (5)	0.2535 (4)	0.3478 (6)	0.080 (3)
C19	0.2736 (6)	0.2075 (6)	0.4288 (7)	0.110 (5)
C20	0.4205 (9)	−0.0693 (10)	0.1618 (6)	0.133 (7)
C21	0.3770 (8)	−0.1304 (8)	0.2302 (9)	0.172 (10)

† Site occupancy = 0.90. ‡ Site occupancy = 0.10.

Table 2. *Selected geometric parameters (Å, °)*

Tb1—O6	2.061 (4)	Tb2—O8	2.520 (4)
Tb1—O4	2.226 (5)	Ti1—O7	1.783 (6)
Tb1—O1	2.281 (6)	Ti1—O8	1.865 (6)
Tb1—O2	2.322 (6)	Ti1—O4	2.021 (5)
Tb1—O5$^{\rm i}$	2.391 (4)	O1—C1	1.423 (10)
Tb1—O8	2.6181 (9)	O2—C2	1.347 (15)
Tb2—O3	2.066 (5)	O3—C3	1.420 (10)
Tb2—O2	2.247 (6)	O4—C4	1.414 (9)
Tb2—O1$^{\rm i}$	2.270 (6)	O5—C5	1.442 (8)
Tb2—O5$^{\rm i}$	2.380 (5)	O6—C6	1.393 (9)
Tb2—O5	2.387 (5)	O7—C7	1.391 (12)
C3—O3—Tb2	172.4 (7)	C7—O7—Ti1	152.6 (7)
C6—O6—Tb1	178.7 (10)		

Symmetry code: (i) $1 - x, -y, z$.

The absolute structure for the compound was chosen according to the Flack (1983) parameter. Site-occupation factors for the Tb and Er atoms were fixed at 0.9 and 0.1, respectively. All H atoms were placed in calculated positions with a common fixed displacement parameter of 0.08 Å^2. Methyl groups were constrained as rigid tetrahedra (C—H 0.98 Å) with H atoms freely rotating around the C—C bonds and riding on the C atoms. Tertiary H atoms were riding on tied C atoms (C—H 1.00 Å).

Data collection: *DIF*4 (Stoe & Cie, 1990). Cell refinement: *DIF*4. Data reduction: *X-RED* (Stoe & Cie, 1996). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AB1489). Services for accessing these data are described at the back of the journal.

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Bis(4-methoxybenzaldehyde thiosemicarbazonato-*S*,*N*^{4})copper(II)

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Abstract

The Schiff base ligand in the title complex, $[\mathrm{Cu}(\mathrm{C_9H_{10}N_3OS})_2]$, lost a proton from its tautomeric thiol form and coordinated to Cu$^{\rm II}$ *via* the mercapto S and β-N atoms. The geometry around Cu$^{\rm II}$ is square planar with two equivalent Cu—N and Cu—S bonds. The two phenyl rings and the coordination moieties are in one plane forming an extensive electronic delocalization system.

Comment

Transition metal organometallic and coordination complexes have emerged as potential building blocks for non-linear optical (NLO) materials due to the various

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