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$[Er_2Al_2(O^iPr)_{12}(HO^iPr)_2]$, a Novel Heterobimetallic Alkoxide

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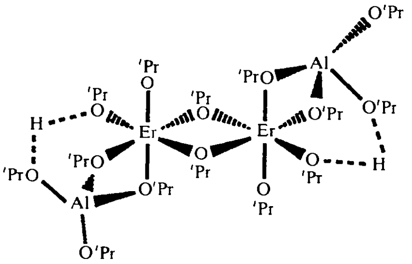
Abstract

A new heterobimetallic tetranuclear alkoxide of the Er–Al system, $[Al_2Er_2(C_3H_7O)_{12}(C_3H_8O)_2]$, has been synthesized and characterized by single-crystal X-ray diffraction and IR spectroscopy. Hexakis(μ_2-isopropoxo)hexakis(isopropoxo)bis(2-propanol)dialuminiumdierbium has the linear composition $[(O^iPr)_2Al]$-(μ_2-$O^iPr)_2$-$[(HO^iPr)Er(O^iPr)]$-(μ_2-$O^iPr)_2$-$[(O^iPr)Er(HO^iPr)]$-(μ_2-$O^iPr)_2$-$[Al(O^iPr)_2]$. The inner pair of Er atoms are each sixfold coordinated and the outer Al atoms are each fourfold coordinated by O atoms. Two intramolecular hydrogen bonds exist between the 2-propanol group at the Er atom and the monodentate isopropoxo ligand at the adjacent Al atom. The adopted chain geometry of four alkoxo-bridged metal atoms is a rather unusual structural feature for heterobimetallic ($M_2M'_2$) alkoxides.

Comment

Alkoxides are important precursors in the organic sol–gel process for the preparation of, for example, construction, opto- and electroceramics (Chandler *et al.*, 1993). The present study is part of a program involving rare earth alkoxides as precursors for anionic conductor ceramics and optical materials for, for example, laser amplifiers and frequency up-conversion devices (Desurvire, 1991). We are presently investigating the formation of alkoxides with various Er-to-Al ratios in the Er–Al–isopropoxide system. These alkoxides are to be used as precursors for the above-mentioned materials. The compounds that have been investigated so far are $[ErAl_3(O^iPr)_{12}]$ and $[Er_5O(O^iPr)_{13}]$ (Wijk *et al.*, 1996, 1998). The title heterobimetallic alkoxide, (I), having an Er:Al composition of 2:2, consists of a linear tetranuclear Al···Er···Er···Al array, with half of the molecule in the asymmetric unit. The central pair of Er atoms are doubly bridged by two isopropoxo groups. Each end of the Er pair is connected to an Al atom *via* bridging isopropoxo groups, forming an $Er_2Al_2O_6$ core in the molecule.



(I)

Although rare, other linear $M_2M'_2$ alkoxides have been characterized by single-crystal X-ray diffraction, namely those of the series $M_2Ge_2(OBu)_8$, M = Co, Ni (Veith *et al.*, 1992). However, these compounds have *tert*-butoxo ligands and tetrahedral coordination around the inner pair of transition metal atoms. Another example of this type of metal-atom arrangement is found in the mixed-valence compound $W_4(\mu\text{-}H)_2(O^iPr)_{14}$ (Akiyama *et al.*, 1981), in which the inner pair of W atoms are octahedrally coordinated in the same way as the Er atoms in the title compound.

The metal-chain structural fragment exhibited by the present compound is not usually adopted by heterobimetallic alkoxides with 2:2 stoichiometry. Instead, a large number of $M_2M'_2$ compounds form a unit with C_{2h} symmetry. This unit, containing two μ_3-O atoms, commonly occurs in this class of heterobimetallic alkoxides (Caulton & Hubert-Pfalzgraf, 1990) and, indeed, the other erbium-pair-containing compound investigated by our group, $[Er_2Ti_4O_2(OEt)_{18}(HOEt)_2]$, exhibits this fragment (Westin *et al.*, 1998).

An Er···Er distance of 3.592 (1) Å indicates that there is no bond between the Er atoms. The Er atoms are coordinated by six O atoms, with an average Er—O distance of 2.27 Å [range 2.040 (2)–2.406 (2) Å]. The Er—O distances increase in the following order: terminal < terminal hydrogen bonded < bridged. The terminally bonded isopropoxo groups on the Er atoms have comparatively short Er—O bonds [2.040 (2) Å] and nearly linear Er—O—C arrangements, having angles of 172.8 (3)°. Isopropoxo groups involved in hydrogen bonding have Er—O—C angles of 131.2 (2)°. The Al atoms each have a pseudo-tetrahedral coordination arrangement of four O atoms, with an average Al—O distance of 1.75 Å [range 1.697 (2)–1.785 (2) Å]. The Al—O distances can be divided into three groups, following the same order of bond distances as for the Er—O bond lengths.

Intermolecular hydrogen bonds are not present in the compound. However, weak to normal intramolecular hydrogen bonding between the donor atom O4, bonded to Er, and the acceptor atom O5, bonded to Al, was inferred from the O4···O5 distance of 2.710 (3) Å. A further indication of this hydrogen bond was the presence of a peak, at reasonable distances from O4 and O5, in the final difference Fourier map. This hydrogen bond can be characterized as linear, asymmetric and non-centred. The bent angle $\alpha_{OH\cdots O}$ of 167 (3)° is in accordance with the donor–acceptor distance (Olovsson & Jönsson, 1976). This non-centred hydrogen bond is probably due to the very significant difference between the Al—O5 and Er—O4 bond lengths. The assumption of a weak to normal hydrogen bond is corroborated by an absorption maximum at 3130 cm^{-1} in the IR spectrum of the compound. The acceptor O atoms on Al exhibit Al—O—C angles of 127.1 (2)°, somewhat smaller than the angle between aluminium and the terminal isopropoxo groups [137.5 (2)°]. Estimated bond-valence sums, 3.12 for erbium and 3.08 for aluminium, confirm the trivalent states of the metal atoms (Brese & O'Keeffe, 1991).

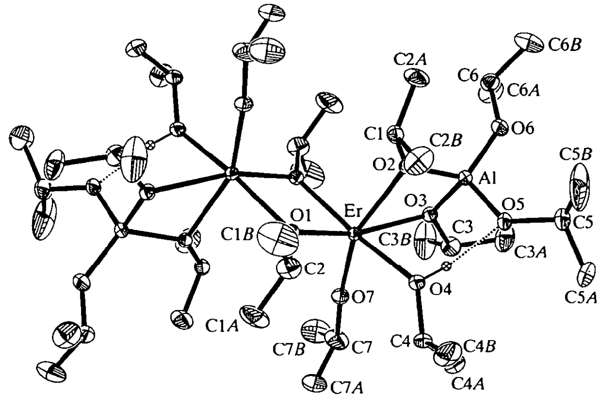


Fig. 1. A perspective view and atomic numbering scheme of the title alkoxide. Probability ellipsoids are drawn at the 30% level. All H atoms, except those participating in hydrogen bonding, have been omitted for clarity.

Experimental

The synthesis of the title complex was performed with extreme precautions against oxygen and water, and the starting materials were all water-free (Wijk *et al.*, 1996). Typically, 15 mmol of potassium was dissolved in 15 ml of 2-propanol–toluene (2:1). To this solution, 5 mmol of $Al(O^iPr)_3$ was added. Two hours later, 5 mmol of $ErCl_3$ was added and the mixture was reacted for 48 h before it was centrifuged. Slow evaporation of the solvent part yielded pink crystals of $[Er_2Al_2(O^iPr)_{12}(HO^iPr)_2]$.

Crystal data

$[Al_2Er_2(C_3H_7O)_{12}(C_3H_8O)_2]$
$M_r = 1217.70$
Triclinic
$P\bar{1}$
$a = 10.797 (3)$ Å
$b = 11.933 (3)$ Å
$c = 12.939 (3)$ Å
$\alpha = 82.457 (1)°$
$\beta = 66.762 (1)°$
$\gamma = 70.985 (1)°$
$V = 1448.2 (6)$ Å^3
$Z = 1$
$D_x = 1.396$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 24 reflections
$\theta = 15.2–18.2°$
$\mu = 2.959$ mm^{-1}
$T = 150 (2)$ K
Irregular
0.40 × 0.35 × 0.25 mm
Pale pink

Data collection

Stoe four-circle diffractometer
$\omega–2\theta$ scans
Absorption correction: by integration (*X-SHAPE*; Stoe, 1996*b*)
$T_{min} = 0.514$, $T_{max} = 0.678$
7157 measured reflections
6309 independent reflections

6084 reflections with $I > 2\sigma(I)$
$R_{int} = 0.013$
$\theta_{max} = 26.99°$
$h = -12 \rightarrow 13$
$k = -15 \rightarrow 15$
$l = -1 \rightarrow 16$
4 standard reflections frequency: 240 min intensity decay: 3.1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.024$
$wR(F^2) = 0.062$
$S = 1.088$
6309 reflections
288 parameters
H atoms: see below

$\Delta\rho_{max} = 1.591$ e Å^{-3}
$\Delta\rho_{min} = -1.335$ e Å^{-3}
Extinction correction: *SHELXL93* (Sheldrick, 1993)
Extinction coefficient: 0.0022 (3)

$w = 1/[\sigma^2(F_o^2) + (0.0366P)^2 + 1.9123P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$

Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters and hydrogen-bonding geometry (Å, °)*

Er—O7	2.040 (2)	Er···Er$^{\rm i}$	3.5918 (7)
Er—O1	2.241 (2)	Al—O6	1.697 (2)
Er—O2	2.346 (2)	Al—O5	1.740 (2)
Er—O3	2.355 (2)	Al—O2	1.774 (2)
Er—O4	2.406 (2)	Al—O3	1.785 (2)
Er···Al	3.2041 (10)		
O7—Er—O1	105.16 (8)	O6—Al—O2	120.38 (11)
O7—Er—O2	156.93 (8)	O5—Al—O2	106.79 (10)
O1—Er—O2	94.94 (7)	O6—Al—O3	119.00 (11)
O1$^{\rm i}$—Er—O2	92.06 (7)	O5—Al—O3	107.40 (10)
O7—Er—O3	94.82 (8)	O2—Al—O3	89.29 (9)
O1—Er—O3	159.11 (7)	O3—Al—Er	46.27 (7)
O1$^{\rm i}$—Er—O3	107.65 (7)	C2—O1—Er	123.8 (2)
O2—Er—O3	64.30 (7)	C2—O1—Er$^{\rm i}$	129.5 (2)
O7—Er—O4	90.89 (9)	Er—O1—Er$^{\rm i}$	106.36 (7)
O1—Er—O4	93.07 (7)	C1—O2—Er	126.1 (2)
O1$^{\rm i}$—Er—O4	161.92 (8)	Al—O2—Er	101.16 (8)
O2—Er—O4	76.62 (7)	C3—O3—Al	125.5 (2)
O3—Er—O4	80.38 (7)	C3—O3—Er	124.7 (2)
O7—Er—Al	124.32 (7)	Al—O3—Er	100.50 (9)
O1—Er—Al	126.04 (5)	C4—O4—Er	131.2 (2)
O6—Al—O5	111.48 (11)		

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O4—H100···O5	0.84 (2)	1.88 (3)	2.710 (3)	167 (3)

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

The position of the H atom participating in hydrogen bonding was determined from the final difference Fourier map and refined isotropically. All other H atoms were refined with fixed isotropic displacement parameters using a riding model. The largest peak and deepest hole in the final difference Fourier map were located 1.15 and 0.83 Å from C7*B* and Er, respectively.

Data collection: *DIF*4 (Stoe, 1990). Cell refinement: *DIF*4. Data reduction: *X-RED* (Stoe, 1996*a*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *XP* (Siemens, 1990). Software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1001). Services for accessing these data are described at the back of the journal.

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A New Phase of Sodium Succinate Hexahydrate

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Abstract

The title compound, $2Na^+.C_4H_4O_4^{2-}.6H_2O$, is made up of chains parallel to the *b* axis, in which Na–[OH_2]$_2$–Na–[$C_4H_4O_2$]–Na–[OH_2]$_2$–Na units are mono-bridged by water molecules. The two central C atoms of the succinate ion are disordered over two positions; the dihedral angles between the carboxylate group and the C—C—C—C backbone in each of its disorder positions are 5.7 (3) and 64.0 (2)°.

Comment

Simple α,ω-dicarboxylate ligands such as oxalate, malonate and succinate are known to exhibit extraordinary versatility in binding metal ions. Many structures of succinates have already been reported. The following univalent cations form non-isostructural salts: Li^+ (Klapper & Küppers, 1973), K^+ (Fonseca *et al.*, 1985), Na^+ (Fonseca