Synthesis, Characterization, and Structural Determination of the Bimetallic Alkoxide $ErAl_3(OC_3H_7^i)_{12}$

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Introduction

In recent, years the demand for new materials with specific properties has increased dramatically, and new preparation routes have therefor been developed. The use of metal alkoxides as precursors for ceramics and thin films is a growing field, especially for heterometallic alkoxides, since they provide a means of better control of the stoichiometry, simpler equipment for manufacture and lower cost. Quite a few heterometallic alkoxides are known, but only a minor part of them are structurally characterized.[1−6] One possible field of application for the mixed metal alkoxides containing Pr, Nd, Eu, Er, and Yb, is for preparing high purity optical materials. The formation of Er−O clusters, which often occur with solid state synthesis and sol−gel processing of Er^{3+} salts, leads to a reduction of the optical activity, and thus the distance between the dopant ions must be kept sufficiently large. The reduction of the optical activity is due to energy transfer between neighboring excited ions, yielding nonradiative relaxation.[7]

Such clustering might be avoided by preparing suitable precursors for a sol−gel process. If an encapsulation of the Er with optically silent alkoxy derivatives, *e.g.* Al, Ti, Zr, Ta, and Nb, can be made and be preserved during the hydrolysis step, clustering can be avoided and higher doping levels can be achieved. The optically silent alkoxy deriviatives surrounding the Er^{3+} are more easily dispersed in the glass precursor of the matrix material (SiO_2−TiO_2). The bimetallic ErAl (1:3) alkoxide is already known, as well as the other corresponding $LnAl_3$ alkoxides.[1,3−6] Cryoscopy, mass spectrometry, and NMR studies have been used to outline the structures of the $LnAl_3(OPr^i)_{12}$ compounds (Ln = lanthanide atom). In these studies it is proposed that all the $LnAl_3(OPr^i)_{12}$ compounds have the same structure, in which Ln is surrounded by three $Al(OPr^i)_4^-$ units, giving a six-coordinated central atom. A related compound, $AlAl_3(OPr^i)_{12}$, has been structurally determined by single crystal diffraction methods[9] and also investigated with the other methods mentioned.[10−12]

Systems of interest to us for thin film preparation of optical materials are $MAl_3(OPr^i)_{12}$, with M = Pr, Nd, Eu, Er, and Yb. Hydrolysis studies are also currently performed on these systems as well as on the related compound with M = Cr, to evaluate if the shielding $Al(OPr^i)_4^-$ shell around Er remains intact and also to evaluate the kinetics and mechanisms of the hydrolysis. The present study is focused on the chemical and structural characterization of $ErAl_3(OPr^i)_{12}$.

Experimental Section

Preparation. All preparations and the mounting of crystals for the X-ray diffraction data collection were performed in a glovebox containing dry, oxygen-free argon atmosphere. The isopropyl alcohol was distilled over CaH_2. The toluene was dried over freshly cut, thin slices of sodium. Commercial $ErCl_3$ (Strem Chemicals) and $Al(OPr^i)_3$ (Sigma) were used. Typically, 0.500 g (12.8 mmol) of potassium was dissolved in 15 mL isopropyl alcohol and 2.612 g (12.8 mmol) of $Al(OPr^i)_3$ was added. After 8 h, 1.166 g (4.26 mmol) $ErCl_3$ and ca 35 mL of toluene were added under stirring, whereafter the reaction was allowed to proceed for 2 days at room temperature, yielding a pink solution and a white precipitate (KCl). The solution was removed and evaporated to dryness. In general, a small amount of K−Al−alkoxide was found together with the $ErAl_3(OPr^i)_{12}$. The dried alkoxide was dissolved in toluene leaving a precipitate of the remaining potassium aluminium isopropoxide. The pink liquid was removed and isopropyl alcohol was added and the liquid was then evaporated in steps until a viscous solution was obtained, from which the crystals grew.

The pink crystals were obtained in a yield of 92% and SEM-EDS analysis revealed no K or Cl. The solubility of these crystals in a 70:30 (by volumes) mixture of $HOPr^i$ and toluene was 0.34 M, while in $HOPr^i$ it was much lower, 0.047 M. In toluene the solubility was 0.62 M and in $Si(OEt)_4$ it was *ca* 0.26 M. The melting point of the compound was 120−2 °C, and the compound is stable up to at least 140 °C and does not decompose for months in solution.

Characterization. The viscous solution and the crystals were hydrolyzed and dried, and the overall metal composition was determined in a scanning electron microscope (SEM, Jeol 820) equipped for energy dispersive analysis of X-ray spectra (LINK AN 10000). FT-IR spectra were recorded on a Bruker IFS55 spectrometer. The solid samples were investigated as KBr tablets and the solutions in a 0.1 mm (mid-IR) or 5 mm (near-IR) quartz cell. UV/vis spectra were recorded in the range 200−900 nm, with a Philips PU8700 spectrophotometer for 0.25 M solutions of $ErAl_3(OPr^i)_{12}$ in a 70:30 mixture of $HOPr^i$ and toluene in 5 mm quartz cells. A Gallenkamp solid block melting point apparatus was used to determine the melting point.

Structure Determination. A few selected crystals were mounted into glass capillaries (ϕ = 0.7 mm) that were melt sealed in the glovebox. Preliminary single-crystal X-ray diffractometer investigations of the finally selected crystal, using Mo Kα radiation, indicated an orthorhombic space group symmetry, $P2_12_12_1$. The crystal had a minor twin component, but as the final results show, the effects from twinning were negligible. Unit cell parameters were determined and refined from the θ-values of 19 accurately centered reflections, as a = 13.150(1), b = 17.404(2), and c = 23.158(3) Å. Single-crystal X-ray diffraction data were collected at room temperature (21 °C) on a Siemens P4/RA diffractometer. Absorption correction was performed for effects of the crystal shape, but the effects from the capillary was neglected. Data were also corrected for background, Lorentz, and polarization effects.

Preliminary erbium atom positions were obtained by conventional heavy atom techniques. The remaining non-hydrogen atomic positions

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Table 1. Crystallographic Data for the Structural Investigation of $ErAl_3(OPr^i)_{12}$[a]

formula: $ErAl_3(OPr^i)_{12}$	volume = 5318.2(13) Å^3
fw = 957.26 g/mol	Z = 4
Space group: $P2_12_12_1$ (No. 19)	calcd density = 1.196 g/cm^3
Unit cell dimensions: a = 13.150(1) Å	μ = 1.69 mm^{-1}
b = 17.464(2) Å	final R = 0.053
c = 23.158(3) Å	final R_w = 0.064

[a] Definitions: $R = \sum[|F(\mathrm{obs}) - F(\mathrm{calc})|]/\sum[F(\mathrm{obs})]$ and $R_w = \sum[|(F(\mathrm{obs}) - F(\mathrm{calc}))|w]/\sum[F(\mathrm{obs})w]$.

Table 2. Selected Intramolecular Distances (Å) and Angles (deg), with Esd's, for $ErAl_3(OPr^i)_{12}$

Distances			
Er1−O1	2.24(2)	Al2−O3	1.79(2)
Er1−O2	2.28(2)	Al2−O6	1.75(2)
Er1−O3	2.20(2)	Al2−O9	1.67(3)
Er1−O5	2.23(2)	Al2−O10	1.66(3)
Er1−O6	2.25(2)	Al3−O1	1.78(2)
Er1−O11	2.24(2)	Al3−O4	1.70(3)
Al1−O2	1.80(2)	Al3−O8	1.65(3)
Al1−O5	1.79(2)	Al3−O11	1.81(2)
Al1−O7	1.68(3)		
Al1−O12	1.66(3)		

Angles			
O1−Er−O2	98.4(6)	O2−Al1−O5	87.7(8)
O1−Er−O3	96.6(6)	O2−Al1−O7	110.2(11)
O1−Er−O5	157.8(7)	O2−Al1−O12	110.4(13)
O1−Er−O6	104.7(6)	O5−Al1−O7	113.4(11)
O1−Er−O11	67.0(6)	O5−Al1−O12	111.3(11)
O2−Er−O3	98.2(6)	O7−Al1−O12	119.4(12)
O2−Er−O5	67.0(6)	O3−Al2−O6	86.4(9)
O2−Er−O6	153.2(6)	O3−Al2−O9	110.1(11)
O2−Er−O11	104.5(6)	O3−Al2−O10	112.2(11)
O3−Er−O5	101.9(6)	O6−Al2−O9	111.2(12)
O3−Er−O6	66.2(6)	O6−Al2−O10	111.8(12)
O3−Er−O11	153.6(6)	O9−Al2−O10	120.1(13)
O5−Er−O6	94.0(6)	O1−Al3−O4	112.2(12)
O5−Er−O11	99.3(7)	O1−Al3−O8	113.4(12)
O6−Er−O11	96.9(6)	O1−Al3−O11	87.2(8)
		O4−Al3−O8	117.6(14)
		O4−Al3−O11	111.8(11)
		O8−Al3−O11	110.7(12)

were found from subsequent calculations of difference electron density ($\Delta\rho$) maps. The hydrogen atoms were positioned by assuming ideal geometry of the alkyl groups and the positions were refined by constraining the C−H distances to 1.0 Å. Due to the large thermal vibrations experienced and the limited accuracy of the isopropoxy group geometries, the O−C$_\alpha$, O−C$_\beta$, and C$_\alpha$−C$_\beta$ bonds were softly constrained. The very large differences in C$_\alpha$−C$_\beta$ distances from the ideal bond length are most likely due to the large thermal vibrations. In the final refinement all the metal and oxygen atoms were allowed to vibrate anisotropically, while the carbon and hydrogen atoms were kept isotropic. To evaluate whether or not the structure model obtained describes the correct enantiomer, the method of Rogers was applied,[13] which refine a parameter that multiplies the imaginary part of the atomic scattering factor. The parameter value +0.92(11) obtained shows that the correct enantiomer is described by the structure model.

Least-squares refinements of the structural model yielded an R value of 0.053 (R_w = 0.064): see Table 1 for further details. The final atomic coordinates with thermal parameters are given as Supporting Information; bond distances and selected bond angles are given in Table 2. The atomic scattering factors used were those for neutral atoms given in ref 14. The SHELXTL program package[15] was used for the crystallographic calculations. For the analysis of molecular pseudosymmetries, routines developed with the MathCAD (Mathsoft Inc. 1994) were used.

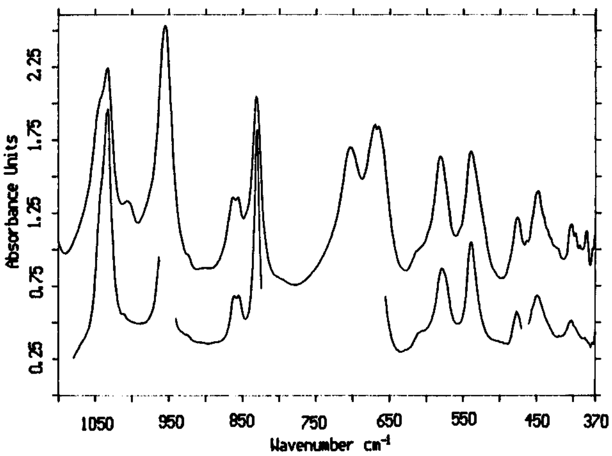

Figure 1. IR spectra of $ErAl_3(OPr^i)_{12}$ in the solid state (upper curve) and dissolved in isopropyl alcohol:toluene (70:30) solvent (lower curve). The plot has been removed where the solvent interactions obscure the spectrum.

Table 3. UV/Vis Bond Maxima for a 0.25 M Solution of $ErAl_3(OPr^i)_{12}$ and Ascribed Transitions from the Ground State $^4I_{15/2}$ of the Er^{3+} Ion

transition	obsd band maxima (cm^{-1} × 10^{-3})	band maxima[18] (cm^{-1} × 10^{-3})
$^2G_{7/2}$	27.94	27.82
$^2K_{15/2}$	27.62	27.58
$^4G_{9/2}$	27.32	27.32
$^4G_{11/2}$	26.43	26.38
$(^2G,^4F)_{9/2}$	24.40	24.48
$^4F_{3/2}$	22.48	22.45
$^4F_{5/2,}$	22.10	22.18
$^4F_{7/2}$	20.63	20.49
$(^2H,^4G)_{11/2}$	19.21	19.01
$^4S_{3/2}$	18.36	18.30
$^4F_{9/2}$	15.36	15.18
$^4I_{9/2}$	12.64	12.35
$^4I_{11/2}$	10.26	10.12
$^4I_{13/2}$	6.57	6.49

Results and Discussion

IR spectra of the compound were recorded both for the crystalline phase and for a 0.25 M in $HOPr^i$:toluene solution (70:30 by volumes). Figure 1 shows the two spectra, covering the region 1170 - 370 cm^{-1}, which contains the M−O and C−O vibrations. There is a striking resemblance between the two spectra, suggesting that the structure of the molecule is very similar in the solid and solution states. The bands in the region <800 cm−$^{-1}$ are assigned to Al−O−Er and Al−O vibration modes, while the bands >800 cm^{-1} can be assigned to different C−O and C-C modes originating from bridging and terminal isopropoxy groups and from the organic part of the ligands.[1,16,17] UV/vis and NIR spectra were recorded for a 0.25 M solution in $HOPr^i$:toluene (70:30). All bands are multiplets and the band maxima and the proposed transitions for each band are given in Table 3. The proposed transitions follow the scheme outlined in ref 18.

The obtained molecular structure is shown in Figure 2, together with the atomic labeling used for the metal and oxygen atoms. The structure determination reveals a molecular formula of $ErAl_3(OPr^i)_{12}$, as proposed by Shiner *et al.*,[3] with the Er being

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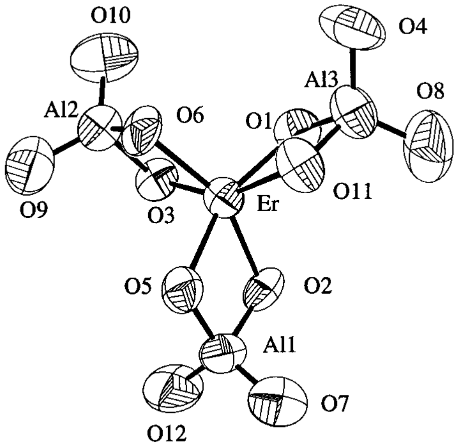

Figure 2. Structure of $ErAl_3(OPr^i)_{12}$, showing 50% probability thermal ellipsoids, with the atomic numbering scheme used. For clarity only the metal and oxygen atoms are included.

coordinated by the oxygen atoms of six bridging isopropoxy groups. Taking the coordination around the oxygen atoms into account, the molecular formula can be written $ErAl_3(\mu_2\text{-}OPr^i)_6(OPr^i)_6$.

The molecule possesses a 3-fold rotation pseudo-symmetry, *i.e.* a noncrystallographically imposed C_3 point symmetry, with the rotation axis perpendicular to the plane through the Al atoms. The deviation from this rotation symmetry is very minor, as the largest deviation of any metal or oxygen atoms from an idealized average structure model with exactly 3-fold symmetry is only 0.13 Å. The Er deviates only 0.03 Å from the centroid of the molecule. The coordination geometry around the Er can be anticipated as a trigonal prism, distorted halfway toward an octahedron. The distortion, described by the angle relating the mutual orientation of the two parallel triangular faces of the prism, is 31°. A 60° distortion angle would give an octahedral coordination. The Al atoms are coordinated by four isopropoxy groups, giving the coordination of a slightly distorted tetrahedron. The coordination tetrahedra are rotated by 24° from the direction of the 3-fold axis.

The bond distances of Er−O are fairly equal, ranging from 2.201 to 2.283 Å, with an average value of 2.244 Å. For the Al−O tetrahedra the bond lengths can be divided into two groups. The longer distances are seen for the bridging μ_2-O, with an average length of 1.792 Å. The other group consists of Al−O bonds of terminal isopropoxy groups, with an average bond length of 1.674 Å. The bond distance distribution and calculated bond valence sums[19] for the metal atoms indicates that all the metal atoms are trivalent. The bond angles (M−O−C) of the bridging isopropoxy groups have an average value of 128.2°, while the bond angles of the terminal isopropoxy groups differ considerably, from 134.3° to 150.8° (average 143.7°). As expected, increasing thermal vibrations are found at the isopropoxy ends, especially so for the terminal groups.

The main features of the structure of $ErAl_3(OPr^i)_{12}$ have previously been proposed for most of the Ln−Al−isopropoxides.[1,3−6] The structure of $AlAl_3(OPr^i)_{12}$ has been determined by single-crystal diffraction methods,[9] and the observed molecular geometry of the compound is related to that of $ErAl_3(OPr^i)_{12}$ with respect to that both have an approximate C_3 symmetry. However, the molecular confirmations differ; *i.e.* in the first case the central Al has an almost ideal octahedral coordination, while the title compound has a distorted trigonal prismatic coordination around the Er. Taking into account the similarities in stereochemical behaviour and in the size of the ionic radii of the central ion, most of the Ln−Al−isopropoxides ought to have a coordination figure around the central ion similar to that of $ErAl_3(OPr^i)_{12}$, rather than to that of $AlAl_3(OPr^i)_{12}$.

The $ErAl_3(OPr^i)_{12}$ molecule, having a single Er encapsulated by optically silent, oxygen bridged Al atoms, fulfils the requirements given above for a precursor to be used in connection with preparation of optical materials. However, the molecule must also retain its structure upon dissolution and upon hydrolysis (*cf.* above). Narula[20] has investigated the hydrolysis pathway of $MAl_3(OPr^i)_{12}$ with M = Ce and La at −78 °C in organic solvents with up to 12 $H_2O/MAl_3(OPr^i)_{12}$ molecules. On the basis of ^1H NMR data, he suggests that the main features of the alkoxide structure persist hydrolysis for addition of 1−6 molecules of H_2O per $MAl_3(OPr^i)_{12}$ unit by incorporation of OH bridges instead of isopropoxy bridges. Preliminary FTIR studies made by us indicate that $ErAl_3(OPr^i)_{12}$ retains its structure upon hydrolysis. Studies of the hydrolysis pathway of $ErAl_3(OPr^i)_{12}$ and studies concerning the use of this molecule as a precursor molecule in connection with preparation of Er-based wave guides are in progress.

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Supporting Information Available: Tables of crystallographic data, positional and anisotropic thermal parameters for the non-hydrogen atoms, positional and isotropic thermal parameters for the hydrogen atoms, and calculated bond distances and angles (5 pages). Ordering information is given on any current masthead page.

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