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Facile formation of luminescent terbium(III) aryloxide complexes directly from terbium metal including the X-ray crystal structures of Tb(OC₆H₃Me₂-2,6)₃(THF)₃ and Tb(OC₆H^{*i*}₃Pr₂-2,6)₃(THF)₂^{\ddagger}

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Abstract

Direct reaction of terbium metal in refluxing isopropanol and phenols provides the luminescent terbium aryloxide species $Tb(OC_6H_3Me_2-2,6)_3(THF)_3$ (1) and $Tb(OC_6H_3^iPr_2-2,6)_3(THF)_2$ (2) in good yield. Crystallographic studies showed 1 to be *fac*-octahedral and 2 to be trigonal bipyramidal with the THF molecules in the axial positions. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The narrow line luminescence of europium and terbium make them important components in energy-efficient optical devices [1]. The continual demand for systems utilizing these metals which have better optical performance at lower cost requires increased efforts to incorporate these elements into optically inert host matrices by easier and more homogeneous methods. Syntheses starting with the elemental metal are highly desirable in this regard compared to ionic metathesis reactions starting with metal salts since they avoid the possibility of contamination with counteranions [2]. Recent studies have shown several ways to generate potential europium precursors directly from the metal [3,4], but little is known about convenient syntheses of soluble terbium complexes directly from the metal. Since terbium metal is less reactive than europium metal, this is more challenging.

We report here that terbium metal can be reacted

directly with isopropanol and 2,6-dialkylphenols in the presence of catalytic amounts of mercury salts to make highly luminescent arene-soluble terbium aryloxide complexes.

2. Experimental

All manipulations were performed under nitrogen with rigorous exclusion of air and water by using Schlenk, vacuum line, and glovebox techniques. Physical measurements were obtained and solvents were purified as previously described [5]. Terbium metal was purchased from Rhone-Poulenc and used as received. Isopropanol was dried over sodium metal. 2,6-Diisopropylphenol was purchased from Aldrich and distilled from 4 Å molecular sieves. 2,6-Dimethylphenol was purchased from Aldrich and sublimed before use. IR spectra were obtained using a Perkin-Elmer series 1600 FTIR spectrophotometer and UV-Vis spectra were obtained using a Shimadzu 160 spectrophotometer. Luminescence measurements were performed on a Hitachi F-4500 spectrometer. Magnetic susceptibility measurements were made following the Evans method [6]. Elemental analyses were performed by Desert Analytics, Tuscon, AZ.

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2.1. $Tb(OC_6H_3Me_2-2,6)_3(THF)_3$ (1)

Isopropanol was vacuum transferred into a 100 ml Schlenk flask containing terbium metal (0.347 g, 2.3 mmol), 2,6-dimethylphenol (0.791 g, 6.8 mmol), HgCl₂ (0.005 g, 0.01 mmol) and $Hg(OAc)_2$ (0.005 g, 0.02 mmol)mmol). The reaction was attached to a Schlenk line and heated at reflux for 48 h. The solvent was removed under vacuum to yield dark green solids. Extraction of the solids with THF and removal of solvent yielded $Tb(OC_6H_3Me_2-2,6)_3(THF)_3$ (1) as a white microcrystalline powder (1.13 g, 66%). Recrystallization of 1 from a toluene-THF mixture at -35°C yielded colorless crystals suitable for X-ray analysis. Anal. Calc. for TbO₆C₃₆H₅₁: Tb, 21.5. Found: Tb, 22.0. χ_{g}^{298} K: 5.35 × 10^{-5} . $\mu_{eff}^{298 \text{ K}}$: 9.7. IR (KBr): 3001 m, 2982 m, 2907 s, 2848 w, 1589 m, 1455 s, 1415 m, 1272 m, 1231 s, 1196 m, 1090 s, 1025 w, 861 m, 761 s cm⁻¹.

2.2. Structure and refinement data for 1

A colorless crystal of approximate dimensions $0.48 \times 0.23 \times 0.20 \text{ mm}^3$ was mounted on a glass fiber and transferred to a Bruker CCD platform diffractometer. The SMART [7] program package was used to determine the unit-cell parameters and for data collection (20 s/frame scan time for a hemisphere of diffraction data). The raw frame data was processed using SAINT [8] and SADABS [9] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL [10] program. The diffraction symmetry was 2/m and the systematic absences were consistent with the centrosymmetric monoclinic space group $P2_1/n$ which was later determined to be correct.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors [11] for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. At convergence, $wR_2 = 0.0937$ and GOF = 1.211 for 388 variables refined against 8284 unique data (as a comparison for refinement on F, $R_1 = 0.0439$ for those 7267 data with $[I > 2\sigma(I)]$).

2.3. $Tb(OC_6H_3^iPr_2-2,6)_3(THF)_2$ (2)

Terbium metal (0.7206 g, 4.4 mmol), 2,6-diisopropylphenol (2.37 g, 13.3 mmol), HgCl₂ (0.005 g, 0.01 mmol) and Hg(OAc)₂ (0.005 g, 0.02 mmol) were reacted in isopropanol as described above for **1**. The dark green solution was worked up by a procedure identical to that of **1** and produced, Tb(OC₆H₃Pr₂-2,6)₃(THF)₂ (**2**) as a microcrystalline white powder (2.66 g, 73%). Recrystallization from toluene at -35° C provided crystals suitable for X-ray analysis. *Anal.* Calc. for TbO₅C₄₄H₆₇: C, 63.30; H, 8.09. Found: C, 63.40; H, 8.07. $\chi_{2}^{298 \text{ K}}$: 4.57 × 10^{-5} . $\mu_{eff}^{298 \text{ K}}$: 9.6. IR (KBr): 3307 m, 3025 w, 2825 s, 2496 w, 1860 m, 1795 m, 1607 s, 1472 m, 1161 s, 1020 m, 890 m, 826 w cm⁻¹.

2.4. Structure and refinement data for 2

X-ray diffraction data on 2 were collected and refined as described above for 1. A colorless crystal of the approximate dimensions $0.50 \times 0.45 \times 0.17$ mm³ was found to have diffraction symmetry of 2/m and the systematic absences were consistent with the centrosymmetric monoclinic space group $P2_1$ which was later determined to be correct. At convergence, $wR_2 = 0.0927$ and GOF = 1.047 for 448 variables refined against 3107 unique data (as a comparison for refinement on *F*, $R_1 = 0.0353$ for those 2910 data with with $[I > 2\sigma(I)]$).

2.5. Luminescence studies

For both 1 and 2, approximately 0.01 mM solutions were prepared in either THF or toluene and transferred to a quartz cell equipped with a 14/20 vacuum adapter. The vessel was removed from the glovebox and transferred to the sample chamber of the spectrometer. Emission data were collected between 250 and 690 nm with excitation between 200 and 680 nm. For 1 in THF, excitation at 285 nm produced emission at 490 and 550 nm. For 1 in toluene, excitation at 295 nm produced emission at 490 and 545 nm. For 2 in THF, excitation at 280 nm produced emission at 485 and 540 nm. For 2 in toluene, excitation at 295 nm produced emission at 490 and 545 nm.

3. Results and discussion

3.1. Synthesis

Terbium metal reacts with 2,6-disubstituted phenols in isopropanol at reflux in the presence of mercury salts to produce solvated tris-aryloxide species in good yield as shown in Eq. (1). The complexes were characterized by IR spectroscopy,

magnetic moment measurement, and elemental analysis. Due to the highly paramagnetic nature of Tb(III) compounds ($\mu_{eff} = 9.4-9.7\mu_B$) [12], X-ray diffraction studies were performed to unambiguously characterize the reaction products. The structures are shown in Figs. 1 and 2.

Reactions in the absence of the mercury salts failed to produce isolable terbium complexes. Attempts to isolate 1 or 2 from the direct reaction of terbium metal, the 2,6-dialkylphenol, and mercuric salts in refluxing THF or toluene were also unsuccessful. This suggests the intermediacy of terbium–isopropoxide species during the course of the reaction. Previous studies of reactions with yttrium and the lanthanide metals with isopropanol at reflux have formed complex structures such as $Y_5O(O'Pr)_{13}$ [13], $Yb_5O(O'Pr)_{13}$ [14], and Nd₆Cl(O'Pr)₁₇ [15]. $Y_5O(O'Pr)_{13}$ has subsequently found to react with Ph₃SiOH to form [Y(OSiPh₃)₃(THF)₃]-(THF) [16]. Step-wise reaction of Tb metal with isopropanol followed by reaction with 2,6-dimethylphenol produced luminescent terbium products, but definitive structural information was not obtained.

3.2. Structural features

The product of the 2,6-dimethylphenol reaction, $Tb(OC_6H_3Me_2-2,6)_3(THF)_3$ (1) crystallizes with a distorted octahedral environment around the terbium and a *fac*-arrangement of the aryloxide and THF ligands.



Fig. 1. Thermal ellipsoid plot of $Tb(OC_6H_3Me_2\text{-}2,6)_3(THF)_3$ (1) with ellipsoids drawn at the 50% probability level.



Fig. 2. Thermal ellipsoid plot of $Tb(OC_6H_3^iPr_2-2.6)_3(THF)_2$ (2) with ellipsoids drawn at the 50% probability level.

This geometry has been observed for the yttrium compound, $Y(OC_6H_3Me_2-2,6)_3(THF)_3$, which crystallized in another space group [17]. Since the yttrium crystals were of poor quality, a detailed description of bond lengths and angles was not available, but high quality metrical data were obtained on **1**. In **1**, the average Tb-O(OAr) distance is 2.132(3) Å, while the average Tb-O(THF) distance is 2.452(3) Å.

The product of the 2,6-diisopropylphenol reaction, Tb(OC₆H₃Pr₂-2,6)₃(THF)₂ (**2**) is isostructural with the Ln(OC₆H₃Pr₂-2,6)₃(THF)₂ (Ln = Er, Lu, Pr, Gd) complexes reported previously [18]. The 2.110(7) Å average Tb-O(OAr) distance in **2** is slightly shorter than the 2.130 Å Gd-O(OAr) average distance as expected based on the difference in ionic radii. The Tb-O(THF) average distance of 2.382(6) Å is equal within error limits to the Gd-O(THF) distance of 2.394(15).

4. Conclusions

These reactions clearly show that luminescent terbium aryloxide products are obtainable directly from the elemental metal and the appropriate phenols. These syntheses avoid the need to dry lanthanide precursors and preclude the possibility of alkali metal or chloride incorporation during preparation.

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