Infinite terbium(III) chains formed from a tetra-phosphorylated resorcinarene cavitand

Hani El Moll, David Sémeril, Dominique Matt, Loïc Charbonnière, Loïc Toupet

All manipulations involving phosphorus derivatives were performed in Schlenk-type flasks under dry nitrogen. Solvents were dried by conventional methods and distilled immediately prior to use. Elemental analyses were performed by the Service de Microanalyse, Institut de Chimie, Université de Strasbourg. Luminescence spectra were recorded on a Horiba Jobin Yvon Fluorolog 3 spectrometer using a 450 W Xe lamp as excitation source. The spectra were recorded in the solid state in 2 mm inner diameter quartz tube. Phosphorescence spectra and decay curves were obtained with a pulsed Xe lamp adapted on the spectrometer. The decay curves were fitted with the FAST program (Version 3, 2006) developed by Edinburgh Instrument Ltd. 5,11,17,23-Tetrakis (diphenylphosphinoylmethyl)-4(24),6(10),12(16), 18(22)-tetramethylenedioxy-2,8,14,20-tetra-pentylresorcin[4]arene 1 was prepared according to the literature procedures.¹

Polymeric \{[\text{Tb}_2(1)(\text{DMSO})_8(\text{CF}_3\text{SO}_3)_2](\text{CF}_3\text{SO}_3)_4\}_n

A solution of 1 (0.100 g, 0.06 mmol) and [\text{Tb}(\text{DMSO})_8](\text{CF}_3\text{SO}_3)_3 (0.148 g, 0.12 mmol) in \text{CH}_2\text{Cl}_2 (30 mL) was stirred for 2h. The solution was then concentrated to ca. 3 mL. Addition of diisopropyl ether (10 mL) afforded a white precipitate (0.195 g, 94 %). Found C 39.71, H 4.55. \text{C}_{122}\text{H}_{164}\text{F}_{18}\text{O}_{38}\text{P}_4\text{S}_{14}\text{Tb}_2\cdot 4\text{CH}_2\text{Cl}_2 (M = 3471.21 + 339.73) requires C 39.77, H 4.76%. Crystals suitable for X-ray diffraction were obtained by slow diffusion of diisopropyl ether into a \text{CH}_3\text{CN} solution of the complex. Formula of the crystals: \text{C}_{134}\text{H}_{168}\text{F}_{18}\text{N}_4\text{O}_{38}\text{P}_4\text{S}_{14}\text{Tb}_2, \text{Mr} = 3675.28, \text{monoclinic, } C2/c, a = 39.2090(10), b = 17.3105(3), c = 29.2837(8)Å, \beta = 122.977(4)°, V = 16673.5(7) Å³, Z = 4, D_X = 1.464 \text{Mg.m}^{-3}, \lambda(\text{MoK} \alpha) = 0.71069Å, \mu = 1.146 \text{mm}^{-1}, F(000) = 7520, T = 100(1) K. The sample (0.24 x 0.12 x 0.12 mm) was studied on an Oxford Diffraction Xcalibur Saphir 3 diffractometer with graphite monochromatized MoK\alpha radiation. The data collection (Crystals, 2004) (2\theta_{\text{max}}= 54°, omega scan frames via 0.7°
omega rotation and 30 s per frame, range HKL: H -50,44  K -21,22  L -26,37) gave 60843 reflections. The data led to 18182 independent reflections from which 9841 with \( I > 2.0\sigma(I) \). The structure was solved with SIR-97,\(^2\) which revealed the non hydrogen atoms of the molecule. After anisotropic refinement, all the hydrogen atoms are found with a Fourier Difference. The whole structure was refined with SHELXL97\(^3\) by the full-matrix least-square techniques (use of \( F \) square magnitude; \( x, y, z, \beta_{ij} \) for Tb, P, C, S, F, O and N atoms, \( x, y, z \) in riding mode for H atoms; 929 variables and 9841 observations with \( I > 2.0\sigma(I) \); calc \( w = 1/[(\sigma^2(Fo^2) + (0.0792 P)^2)] \) where \( P = (Fo^2 + 2Fc^2)/3 \) with the resulting \( R = 0.061, R_W = 0.164 \) and \( S_W = 0.960, \Delta\rho < 2.4 \text{ eÅ}^{-3} \). The asymmetric unit of the complex is composed of half of a cavitand, one terbium ion coordinated to four molecules of DMSO and a triflate ion, two free triflate anions, and four half-occupancy acetonitrile molecules, two in general positions, one on a twofold axis and one disordered about a twofold axis with the N atom on the twofold axis. Crystallographic data for this structure have been deposited with the Cambridge Crystallographic Data Centre under deposition number 634846. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

**Fig. S-1** Molecular structure of \([\text{[Tb}_2(1)\text{(DMSO)}_8\text{(CF}_3\text{SO}_3)_2]\text{(CF}_3\text{SO}_3)_4\}_{n}\)

**Fig. S-2** Infrared spectrum of the terbium complex after recrystallisation from \(\text{CH}_2\text{Cl}_2\cdot\text{iPr}_2\text{O}\).