^{1}H NMR spectroscopic study of paramagnetic lanthanide(III) texaphyrins. Effect of axial ligation.

Autorzy

Jerzy Lisowski

Jonathan L. Sessler

Vincent Lynch

T. D. Mody

Rok wydania

1995

Czasopismo

Journal of the American Chemical Society

Numer woluminu

117

Strony

2273-2285

DOI

10.1021/ja00113a016

Kolekcja

Naukowa

Język

Angielski

Typ publikacji

Artykuł

Streszczenie

Paramagnetic Ce(ffl), ( ), Nd(EI), Sm(ni), ( ), Tb(m), Dy(ffl), ( ), Er(EI), Tm(m), and Yb(m) texaphyrins were studied in solution using NMR spectroscopic techniques. Key spectroscopic features for the dinitrate complexes LnTxfNOa): were assigned on the basis of ID NOE, COSY, and ROESY experiments as well as line width and isotropic shift analysis. The observed isotropic shifts can be fit to theoretical models, assuming dipolar contributions are dominant for all but the imino protons. The resulting calculated values are consistent with highly rhombic magnetic susceptibility tensors for those paramagnetic lanthanide texaphyrins in which one of the

molecular magnetic axes is roughly perpendicular to the macrocycle plane. For the dinitrate complexes, a change in the magnetic anisotropy was observed between the ( ) and Er(Ell) texaphyrin complexes, a phenomenon that is considered reflective of the changes in metal-centered axial ligation that occur as the lanthanide series is transversed. The derived contact shifts of the imino protons were found to follow well the expected theoretical dependence on (Sz). Exchange of both axial nitrate anions for phosphate-type ligands, confirmed by solution phase titration studies, brings about a drastic change in the observed spectral patterns. These changes can be accounted for fully by altering the magnetic susceptibility tensor so as to accommodate what are presumed to be changes in the effective crystal field parameters. Conformation of phosphate coordination in the solid state came from a single crystal X-ray diffraction

analysis of the bis(diphenyl phosphate) adduct of Dy(III) texaphyrin. Crystals of (Cg^gNsCyDyffCeHslz-PC^kO.MfCHaOH) (DyTx(Pl)2), obtained by diffusion of diphenyl phosphate into methanolic DyTxfNOsh solution, were triclinic, space group PI, with a = 14.482(3), b = 14.664(3), and c = 15.580(3) Á, a = 69.544(15), ß = 65.695(15), and =

70.377(15)°, V = 2751.1(11) Á* 123, Z = 2, gcalc = 1.48 g/cnT3. The structure refined to a final RCF2) = 0.109 for 644 parameters using 8390 reflections. The Dy(III) ion is seven-coordinate with five donor atoms being provided by the texaphyrin ligand and two by monodentate diphenyl phosphate ions. The Dy(III) ion is only 0.073 Á from the plane through the five nitrogen atoms of the macrocycle. The Dy(III)—O bond lengths are equivalent
and average 2.228(5) Á. The Dy—Npyrroie bond lengths average 2.363(3) Á while the Dy—N¡mine bond lengths average
2.448(4) A.

Adres publiczny

https://doi.org/10.1021/ja00113a016

Strona internetowa wydawcy

https://www.acs.org/content/acs/en.html