Helical Structures

DOI: 10.1002/ange.200602060

Structurally Characterized Quadruple-Stranded Bisbidentate Helicates**

*Jide Xu and Kenneth N. Raymond**

Although examples preceded the definition, the term "helicate" was introduced by Lehn et al. in 1987 for metal complexes that contain two or more metal centers bridged by one or more ligand strands.[1] Helicates are the simplest and most fundamental supramolecular architectures.[2–3] The formation of different types of helicates is a consequence of the combination of the information intrinsic to the helicate components. Since this self-assembly process is also the basis for the formation of other supramolecular architectures and devices, helicates in particular have received much attention.[2–3] For example, early work in this laboratory on M^{III} triple-stranded helicates[4] elucidated structural principles that have allowed the development of a versatile class of inorganic supramolecular structures.[5] While numerous single-, double-, and triple-stranded helicates have been well documented,[2–4,6] there are only a few examples of quadruple-stranded helicates,[7–9] as a result of the increased complexity of this architecture in relation to other helicates.

As predicted,[2] most reported saturated quadruple-stranded helicates have been achieved by employing a combination of square-planar metal centers with oligomonodentate bridging ligands.[8] Recently, the formulation of the first quadruple-stranded bisbidentate helicate was confirmed[9] by electrospray mass spectrometry as a double-charged anion, which was composed of two Eu^{III} ions and four bis(β-diketone) ligands. However, there have been no reports of fully characterized fourfold-symmetric oligobidentate quadruple-stranded helicates, nor reports of quadruple-stranded actinide helicates. The design and synthesis of oligobidentate quadruple-stranded helicates has remained a challenge.

A continuing goal in our group has been the development of chelating agents for lanthanide and actinide ions.[10] The lanthanide and actinide ions generally display high, variable (8, 9, or higher) coordination numbers which makes them excellent candidates for matching the coordination require-

---

[*] Dr. J. Xu, Prof. K. N. Raymond
Department of Chemistry
University of California
Berkeley, CA 94720-1460 (USA)
Fax: (+1) 510-486-5283
E-mail: raymond@socrates.berkeley.edu

[**] Coordination Number Incommensurate Cluster Formation part 33. This research was supported by the Director, Office of Science, Office of Advanced Scientific Computing Research, Office of Basic Energy Sciences (U.S. Department of Energy) under contract DE-AC02-05CH11231. The authors would like to thank Modi Wetzler, Matt Stavis, Geza Szigethy, Dr. Christoph Jocher, and Dr. Michael Seitz for helpful discussions and suggestions.

ment (8 or higher) of oligobidentate quadruple-stranded helicates. Indeed, the high coordination number of lanthanide and actinide ions potentially permits greater versatility in the design and construction of supramolecular edifices, of which quadruple-stranded helicates represent the important first step. However, the high and variable coordination number also presents a challenge along with complicated coordination geometries.

It has been suggested[2] that the synthesis of a quadruple-stranded helicate might be achieved by employing a combination of square-antiprismatic metal centers with oligobidentate bridging ligands. A metal ion with fourfold coordination geometry, such as square antiprism or monocapped square antiprism, would be a good candidate for a saturated quadruple-stranded helicate. However, quadruple-stranded helicates based on eight-coordinate square-antiprism metal ions may leave relatively large openings at both ends of the helicate, thus causing undesirable high repulsion energy between the donor atoms (Figure 1 a). As a result, we concluded that nine-coordinate metal ions, with monocapped square-antiprism geometry, in which the donors are distributed more evenly around the central metal ion, would be the better choice for designing a quadruple-stranded helicate (Figure 1 b).

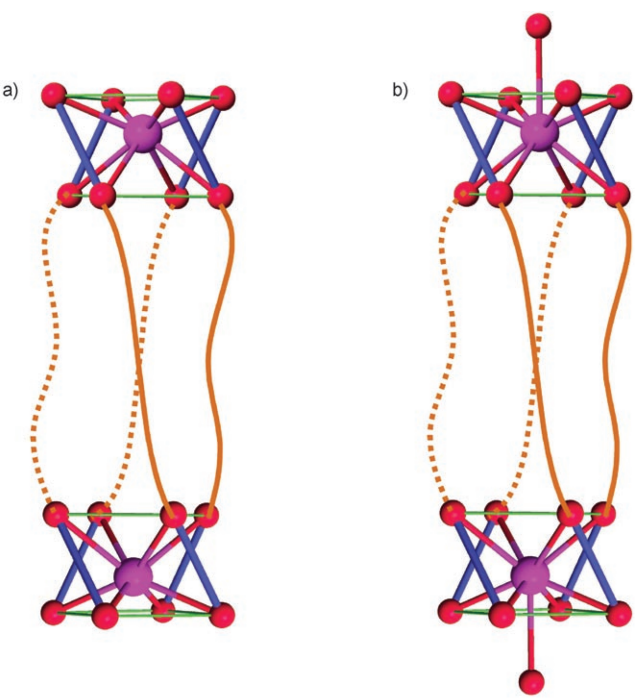
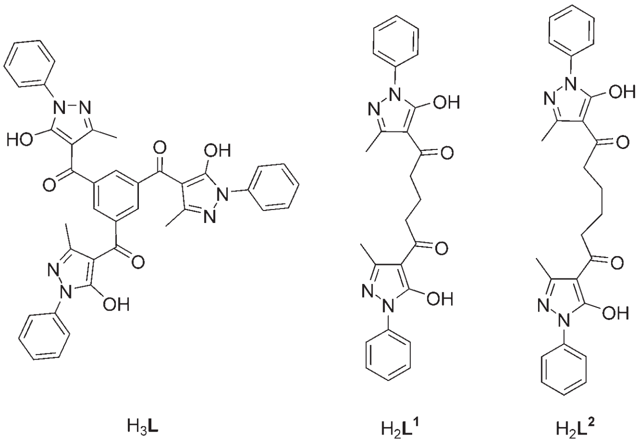


Figure 1. Schematic view of quadruple-stranded helicates based on a) square-antiprism (C.N.: 8) and b) monocapped square-antiprism (C.N.: 9) metal centers (purple, donor atoms red) and bisbidentate ligand strands (orange). C.N. = coordination number.

We previously reported that the tris-β-diketonate type hexadentate 4-acyl-2-pyrazolin-5-one ligand, $H_3\mathbf{L}$ (Scheme 1), forms a supramolecular lanthanide complex $[La_8\mathbf{L}_8]$.[11] The bisbidentate 4-acyl-2-pyrazolin-5-one ligands were first synthesized about two decades ago.[12] The avidity of 4-acyl-2-pyrazolin-5-one ligands towards lanthanide and actinide ions has long been recognized.[13] One such bisbidentate ligand $H_2\mathbf{L}^1$ (Scheme 1), for example, forms triple-stranded dinuclear lanthanide complexes $[Ln_2(\mathbf{L}^1)_3(dmf)_4]$ (dmf = *N*,*N*,-dimethylformamide), in which each lanthanide ion is eight-coordinate with three bidentate ligand moieties and two solvent DMF molecules.[13] It was therefore reasoned that these bisbidentate pyrazolonate ligands, in combination with eight- or nine-coordinate tetravalent ions, such as Th^{IV}, would lead to quadruple-stranded helicates, because the high charge (4+) would encourage four monoanionic bidentate pyrazolone ligand moieties to bind at each central metal ion. In addition, repulsion energy calculations predicted that the capped square antiprism isomer with a C_4 symmetry axis is the discrete potential energy minimum for $[M^{IV}(bidentate)_4(monodentate)]$ complexes.[14,15] In such a geometry, the monodentate ligand occupies the cap position and the four equivalent bidentate ligands are wrapped around the nine-coordinate M^{IV} atoms, thus forming capped square antiprisms with the bidentate ligands spanning the edges linking the two square faces of the square antiprism (Figure 1 b).



Scheme 1. Tris-β-diketonate $H_3\mathbf{L}$ and bis-diketonate 4-acyl-2-pyrazolin-5-one ligands $H_2\mathbf{L}^1$ and $H_2\mathbf{L}^2$ with three and four methylene linear scaffolds, respectively.

A series of bisbidentate pyrazolone ligands with systematically varied lengths of the linear ligand scaffold was prepared according to reported procedures.[12,13] Scheme 1 shows two examples, $H_2\mathbf{L}^1$ and $H_2\mathbf{L}^2$, with a linear scaffold of three and four methylene groups, respectively.

The Th^{IV} quadruple-stranded helicate complexes were prepared by treatment of Th^{IV} tetrakisacetylacetonate with two equivalents of bisbidentate pyrazolone ligands $H_2\mathbf{L}^1$ or $H_2\mathbf{L}^2$ in a solution of MeOH/$CHCl_3$ (1:1). FAB(+) mass spectrometric analysis indicated that both Th^{IV} complexes have the expected $M_2\mathbf{L}_4$ stoichiometry. The ^1H NMR spectra of these complexes in $[D_6]$DMSO are consistent with the formation of highly symmetrical quadruple-stranded helicates with average D_4 symmetry on the NMR timescale. For example, the ^1H NMR spectrum of $[Th_2(\mathbf{L}^1)_4]$ shows only one multiplet for the protons of the central methylene units of the ligand (Figure 2, upper panel). After crystallization from

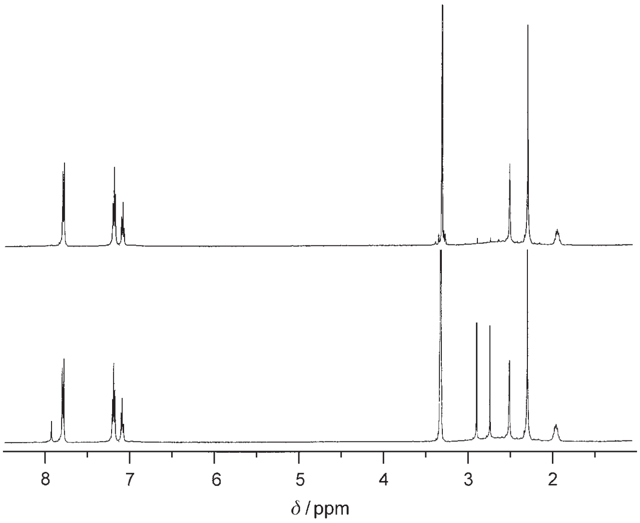


Figure 2. Proton NMR spectra of a$[Th_2(\mathbf{L}^1)_4]$ (upper panel) and $[Th_2(\mathbf{L}^1)_4(dmf)_2]$ (lower panel) in $[D_6]$DMSO.

DMF, the NMR spectra of the complex indicated the presence of two DMF molecules associated with the complex, and only one set of the DMF peaks is apparent (Figure 2, lower panel). The high symmetry of the original molecule is retained, which implies that the two DMF molecules are located on the C_4 axis, at the termini of the helicate, as it seems unlikely that full scrambling at the position of the bisbidentate ligand occurs on the NMR timescale.

As a result of the high nuclear quadrupole moment of thorium (Q(mbarn) = 4300),[16] the NMR signals of the ligand spacer methylene groups adjacent to the thorium coordination centers are broadened and can be detected only at elevated temperatures (Figure 3).

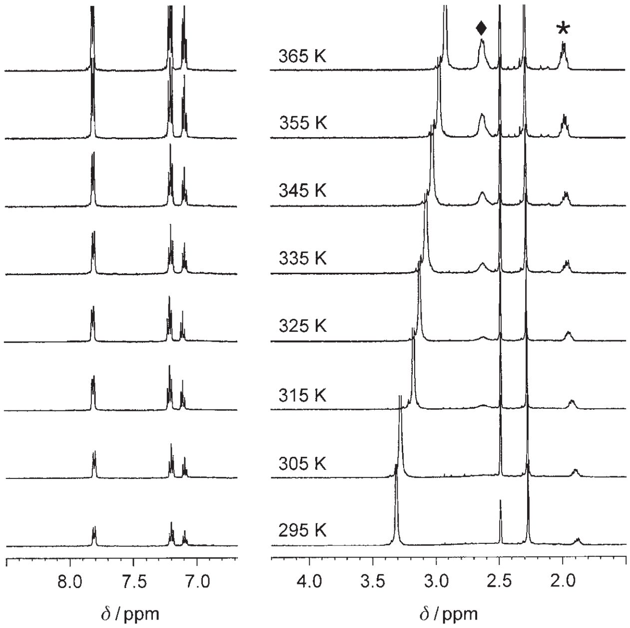


Figure 3. Variable-temperature NMR spectra of $[Th_2(\mathbf{L}^1)_4]$ in $[D_6]$DMSO. The signal labeled with the diamond represents the central methylene, and the star represents the methylene groups of the scaffold adjacent to the coordination centers.

Single-crystal X-ray structure analyses were carried out to determine the solid-state structures of $[Th_2(\mathbf{L}^1)_4]$ and $[Th_2(\mathbf{L}^2)_4]$.[17] X-ray quality crystals of $[Th_2(\mathbf{L}^1)_4(dmf)_2]$ were grown by slow evaporation of its wet DMF solution (1 % H_2O in DMF), while those of $[Th_2(\mathbf{L}^2)_4(dmf)_2]$ were grown from wet DMF solution by diffusion of diethyl ether. The crystal structures of both helical complexes are shown in Figures 4 and 5. These structures indicate that both of the quadruple helicates are homochiral, which implies that there might be mechanical coupling between the two centers of each helicate such that the chirality at one can be transmitted to the second.[2]

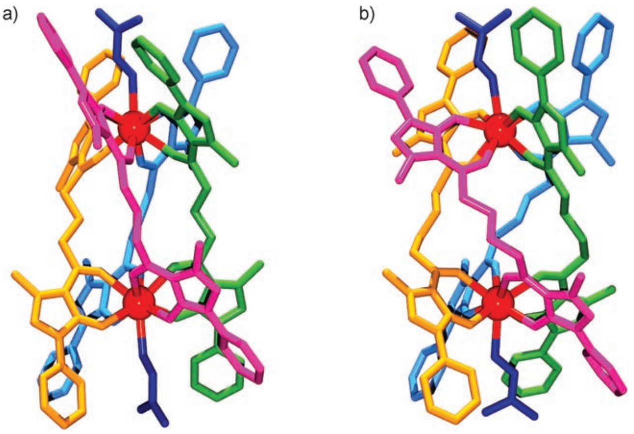


Figure 4. Frame-and-sphere representations of the crystal structure of a) $[Th_2(\mathbf{L}^1)_4(dmf)_2]$ and b) $[Th_2(\mathbf{L}^2)_4(dmf)_2]$ as viewed perpendicular to the twofold axis of the quadruple-stranded helicate. For clarity, each ligand is represented in a different color, with thorium ions represented by dark red spheres, coordinated dmf dark blue.

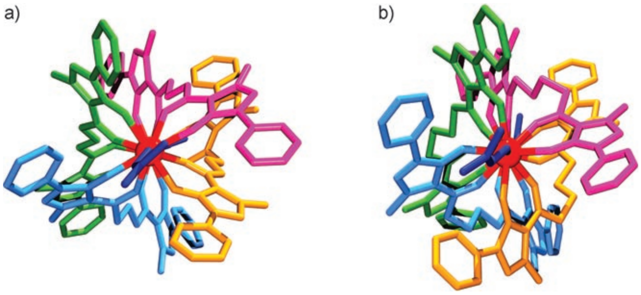


Figure 5. Frame-and-sphere representations of the crystal structure of a) $[Th_2(\mathbf{L}^1)_4(dmf)_2]$ and b) $[Th_2(\mathbf{L}^2)_4(dmf)_2]$ as viewed down the fourfold axis of the quadruple-stranded helicate. For clarity, each ligand is represented in a different color, with thorium ions represented by dark red spheres, coordinated dmf dark blue.

In both helicates, $[Th_2(\mathbf{L}^1)_4(dmf)_2]$ and $[Th_2(\mathbf{L}^2)_4(dmf)_2]$, the Th^{IV} ions are nine-coordinate. This coordination number has several idealized coordination geometries. The tricapped trigonal prism (D_{3h}) and capped square antiprism (C_{4v}) are the most stable geometries, and the energy difference between the two is very small as predicted by repulsion energy calculations.[14,15] We thus employed the shape measure S to assess this subtle difference[18] and found that in both helicates the nine-coordinate geometries can be assigned as being closest to the monocapped square antiprism (C_{4v}) based on the shape measure calculation.

As expected from repulsion energy calculations and previous observations,[14,15] the bidentate units are symmetrically bonded in a capped square-antiprism geometry (Figure 1 b), with the donor atoms that form the capped face (O_{cf}) experiencing considerably less repulsion than those that form the uncapped face (O_{uf}), in agreement with the observed average Th–O lengths in the quadruple helicates. The Th^{IV}–O_{cf} bond lengths are 2.41(1) and 2.40(1) Å and the Th^{IV}–O_{uf} bond lengths are 2.47(3) and 2.48(3) Å in $[Th_2(\mathbf{L}^1)_4(dmf)_2]$; the Th–$O_{cf}$ bond lengths are 2.38(3) and 2.41(2) Å and the Th–O_{uf} bond lengths are 2.49(6) and 2.47(2) Å in $[Th_2(\mathbf{L}^2)_4(dmf)_2]$. Note that in the 10-coordinate Th^{IV} complex of bis(4-benzoyl-2,4-dihydro-5-methyl-2-phenyl-3-*H*-pyrazolonato-*O*,*O*′)-bis(nitrato-*O*,*O*′)-bis(triphenylphosphine oxide-*O*) complex,[19] the bond lengths between the Th^{IV} ion and the two oxygen donors of a bidentate 4-acyl-pyrazolonate ligand are quite similar at 2.435 and 2.447 Å, respectively.

The pitch *L* of a helicate is defined by Equation 1,[2] where *d* is the distance (Å) between the upper and bottom surfaces

$$L = d/(\omega_1/360) \tag{1}$$

of the helicate cylinder and ω_1 is the twist angle (in degrees) of the upper and bottom surfaces. An ideal helicate should be palindromic (constant pitch), which is not the case with $[Th_2(\mathbf{L}^1)_4(dmf)_2]$ and $[Th_2(\mathbf{L}^2)_4(dmf)_2]$, and three subpitches L_1, L_2, and L_3 compose the total pitch L_T (Figure 6). The two subpitches (L_1 and L_3) of both capped square antiprisms of the helicate are different from that of the bridging part (L_2; see Table 1).

Previous studies have found that the stereoselective formation of triple-stranded helicate complexes from linear alkyl-bridged ligands depends, to a large extent, on the preferred conformation of the spacers. An odd number of methylene units yields a molecule with an internal mirror plane, thus producing an achiral *meso* helicate. In the case of an even number of methylene units, the favored conformation imposes a C_2 axis upon complex formation and will lead to a chiral helicate.[3] In the case of bisbidentate quadruple-stranded helicate complexes formed from linear alkyl-bridged ligands, the preferred conformation of the spacer does not significantly affect the stereochemistry of the complexes. With both three and four (odd or even) methylene spacers, the complexes are all homochiral helicates. However, the alkyl-bridge pitch (L_2) in $[Th_2(\mathbf{L}^1)_4(dmf)_2]$ ($n=3$, odd) is much longer than that in $[Th_2(\mathbf{L}^2)_4(dmf)_2]$ ($n=4$, even), which suggests a trend similar to that observed in the triple-stranded helicates. Given the important role of chirality in the application of supramolecular compounds in catalysis, the difference between the observed behavior of the triple- and quadruple-helicate complexes is significant.

In summary, new actinide quadruple-stranded helical supramolecular architectures have been synthesized in which two capped square-antiprismatic Th^{IV} centers are coordinated by four bisbidentate 4-acylpyrazolone chelating strands. These complexes are the first two structurally characterized examples of bisbidentate quadruple-stranded helical complexes and are another remarkable example of cluster formation by incommensurate coordination number. These helicates and the previous $[La_8\mathbf{L}_8]$ complex ("The Lord of Rings")[11] highlight the versatility of 4-acylpyrazolone ligands in lanthanide and actinide coordination chemistry, with implications ranging beyond the field of supramolecular chemistry.

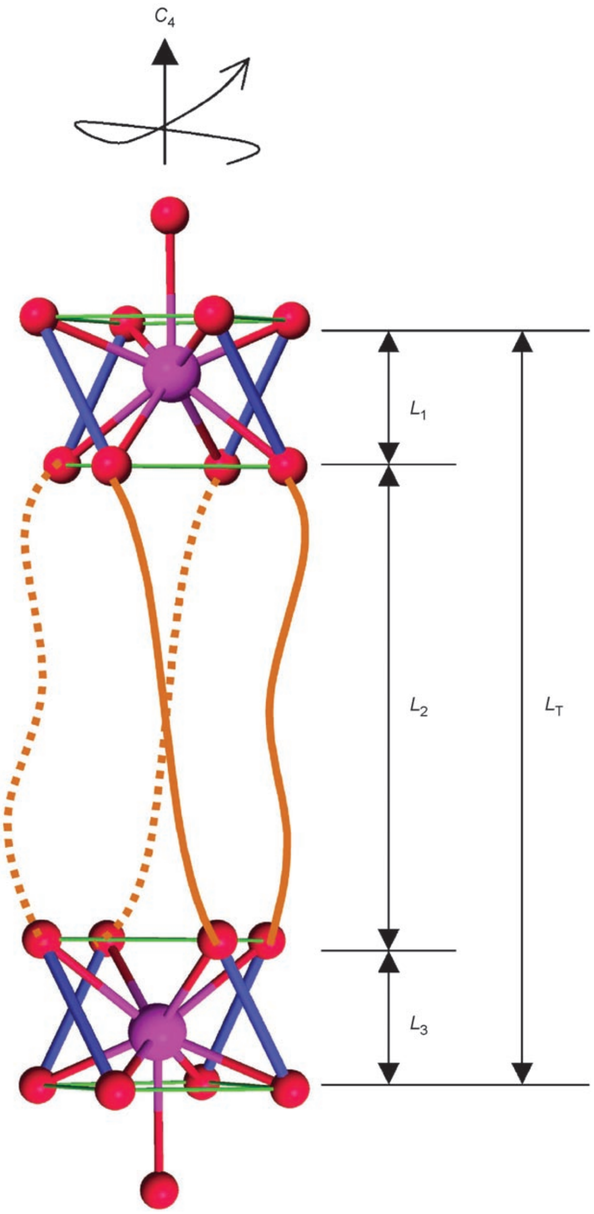


Figure 6. Different subpitches (L_1–L_3) in a quadruple-stranded helicate, in which the height of the helicate (L_T) is defined as the distance between the centroids of the outer square faces. Colors as in Figure 1. The thick edges of the polyhedra represent the bidentate spanning edges.

Experimental Section

$[Th_2(\mathbf{L}^1)_4]$: A solution of $[Th(acac)_4]$ (acac = acetylacetone; 0.05 mmol) in absolute methanol (10 mL) was added to a solution of $H_2\mathbf{L}^1$ (0.11 mmol) in $CHCl_3$ (10 mL). The reaction mixture was

Table 1: Twist angles and helical pitches in $[Th_2(\mathbf{L}^1)_4(dmf)_2]$ and $[Th_2(\mathbf{L}^2)_4(dmf)_2]$.

Complex	$[Th_2(\mathbf{L}^1)_4(dmf)_2]$	$[Th_2(\mathbf{L}^2)_4(dmf)_2]$
Th(1)–Th(2) distance (Å)	8.304	8.151
Height of the upper square antiprism (Å)	2.367	2.328
Average twist angle of the upper square antiprism (°)	40.5	43.8
Pitch of the upper square antiprism L_1 (Å)	21.04	19.13
Height of the alkyl bridge (Å)	5.282	5.206
Average twist angle of the alkyl bridge (°)	4.3	37.5
Pitch of the alkyl bridge part L_2 (Å)	442.21	49.98
Height of the bottom square antiprism (Å)	2.367	2.376
Average twist angle of the lower square antiprism (°)	40.5	39.5
Pitch of the bottom square antiprism L_3 (Å)	21.04	21.65
Average total twist angle (°)	85.2	120.6
Distance between the outer faces of upper and lower square antiprisms (Å)	10.01	9.86
Total pitch L_T (Å)	42.3	29.6

heated at reflux under N_2 with stirring for 16 h, during which time a beige precipitate formed. The solid was collected by filtration, washed with methanol, and dried under vacuum to yield 88 mg (0.039 mmol, 78%) of $[Th_2(\mathbf{L}^1)_4]$ based on $[Th(acac)_4]$. Elemental analysis (%) calcd for $C_{100}H_{88}N_{16}O_{16}Th_2$ (2233.99 $g\,mol^{-1}$): C 53.76, H 3.97, N 10.03; found: C 53.47, H 4.11, N 10.22; ^1H NMR (500 MHz, $[D_6]$DMSO, 25 °C): $\delta = 1.93$ (qt, 8H, $J = 7.0$ Hz; CH_2), 2.27 (s, 24H; CH_3), 7.09 (t, $J = 7.5$ Hz, 8H; ArH), 7.20 (t, $J = 7.7$ Hz, 16H; ArH), 7.80 ppm (d, $J = 8.0$ Hz, 16H; ArH); (+)FAB-MS $[MH^+]$ m/z 2193.7. This compound was recrystallized from wet DMF (containing 1% H_2O) to provide X-ray-quality colorless crystals of $[Th_2(\mathbf{L}^1)_4(dmf)_2]\cdot 6\,DMF\cdot 0.5\,H_2O$.

$[Th_2(\mathbf{L}^2)_4]$: This compound was prepared by a similar procedure as above, except $H_2\mathbf{L}^2$ was used instead of $H_2\mathbf{L}^1$, and yielded 84 mg (0.037 mmol, 74%) based on $[Th(acac)_4]$. Elemental analysis (%) calcd for $C_{104}H_{96}N_{16}O_{16}Th_2$ (2290.05 $g\,mol^{-1}$): C 54.55, H 4.23, N 9.79; found: C 54.22, H 4.33, N 9.82; ^1H NMR(500 MHz, $[D_7]$DMF, 25 °C): $\delta = 1.20$ (s, br, 8H, CH_2), 1.92 (s, br, 8H, CH_2), 2.41 (s, 24H, CH_3), 7.09 (t, $J = 7.5$ Hz, 8H, ArH), 7.22 (t, $J = 7.7$ Hz, 16H, ArH), 7.94 ppm (d, $J = 8.0$ Hz, 16H, Ar H); (+)FAB-MS $[MH^+]$ m/z 2289.6. Colorless X-ray-quality crystals $[Th_2(\mathbf{L}^2)_4(dmf)_2]\cdot 0.5\,DMF\cdot 1.5\,C_4H_{10}O$ were obtained form diffusion of its DMF solution into diethyl ether.

Received: May 23, 2006

Keywords: actinides · helical structures · self-assembly · shape analysis · supramolecular chemistry

---

[1] J.-M. Lehn, A. Rigault, J. Siegel, J. Harrowfield, B. Chevrier, D. Moras, *Proc. Natl. Acad. Sci. USA* **1987**, *84*, 2565–2569.

[2] C. Piguet, G. Bernardinelli, G. Hopfgartner, *Chem. Rev.* **1997**, *97*, 2005–2062; J.-C. G. Bünzli, C. Piguet, *Chem. Rev.* **2002**, *102*, 1897–1928, and references therein.

[3] a) M. Albrecht, *Chem. Rev.* **2001**, *101*, 3457–3497; b) M. Albrecht, *Chem. Soc. Rev.* **1998**, *27*, 281–288, and references therein.

[4] R. C. Scarrow, D. L. White, K. N. Raymond, *J. Am. Chem. Soc.* **1985**, *107*, 6540–6546.

[5] a) A. V. Davis, K. N. Raymond, *J. Am. Chem. Soc.* **2005**, *127*, 7912–7919; b) D. Fiedler, R. G. Bergman, K. N. Raymond, *Angew. Chem.* **2006**, *118*, 759–762; *Angew. Chem. Int. Ed.* **2006**, *45*, 745–748; c) D. H. Leung, D. Fiedler, R. G. Bergman, K. N. Raymond, *Angew. Chem.* **2004**, *116*, 981–984; *Angew. Chem. Int. Ed.* **2004**, *43*, 963–966; d) D. L. Caulder, K. N. Raymond, *J. Chem. Soc. Dalton Trans.* **1999**, 1185–1200; e) T. Beissel, R. E. Powers, K. N. Raymond, *Angew. Chem.* **1996**, *108*, 1166–1170; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1084–1086.

[6] a) E. C. Constable in *Comprehensive Supramolecular Chemistry, Vol. 9* (Eds.: J.-M. Lehn, J.-P. Sauvage, M. W. Hosseini), Pergamon, Oxford, **1996**, p. 213; b) A. Williams, *Chem. Eur. J.* **1997**, *3*, 15–19; c) A. E. Rowan, R. J. M. Nolte, *Angew. Chem.* **1998**, *110*, 65–71; *Angew. Chem. Int. Ed.* **1998**, *37*, 63–68, and references therein.

[7] a) S. J. Shieh, C. C. Chou, G. H. Lee, C. C. Wang, S. M. Peng, *Angew. Chem.* **1997**, *109*, 57–59; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 56–59; b) A. F. Cotton, L. M. Daniels, G. T. Jordan, C. A. Murillo, *J. Am. Chem. Soc.* **1997**, *119*, 10377–10381; c) Y.-H. Chen, C.-C. Lee, C.-C. Wang, G.-H. Lee, S.-Y. Lai, F.-Y. Li, C.-Y. Mou, S.-M. Peng, *Chem. Commun.* **1999**, 1667–1668; d) H. A. Burkill, R. Vilar, A. J. P. White, D. J. Williams, *J. Chem. Soc. Dalton Trans.* **2002**, 837–839.

[8] a) L. J. Barbour, G. W. Orr, J. L. Atwood, *Nature* **1998**, *393*, 671–673; b) D. A. McMorran, P. J. Steel, *Angew. Chem.* **1998**, *110*, 3495–3497; *Angew. Chem. Int. Ed.* **1998**, *37*, 3295–3297; c) P. N. W. Baxter, J.-M. Lehn, G. Baum, D. Fenske, *Chem. Eur. J.* **2000**, *6*, 4510–4517; d) C.-Y. Su, Y.-P. Cai, C.-L. Chen, H.-X. Zhang, B.-S. Kang, *J. Chem. Soc. Dalton Trans.* **2001**, 359–361; e) T. D. Owens, F. J. Hollander, A. G. Oliver, J. A. Ellman, *J. Am. Chem. Soc.* **2001**, *123*, 1539–1540; S. L. Castro, O. Just, W. S. Rees, Jr., *Angew. Chem.* **2000**, *112*, 963–965; *Angew. Chem. Int. Ed.* **2000**, *39*, 933–935.

[9] A. P. Basset, S. W. Megennis, P. B. Glover, D. J. Lewis, N. Spencer, S. Parsons, R. M. Williams, L. De Cola, Z. Pikramenou, *J. Am. Chem. Soc.* **2004**, *126*, 9413–9424.

[10] a) A. E. V. Gorden, D. K. Shuh, B. E. F. Tiedemann, R. E. Wilson, J. Xu, K. N. Raymond, *Chem. Eur. J.* **2005**, *11*, 2842–2848; b) S. Petoud, S. M. Cohen, J.-C. G. Bünzli, K. N. Raymond, *J. Am. Chem. Soc.* **2003**, *125*, 13324–13325; c) J. Xu, D. W. Whisenhunt, Jr., A. C. Veeck, C. U. Linda, K. N. Raymond, *Inorg. Chem.* **2003**, *42*, 2665–2674.

[11] J. Xu, K. N. Raymond, *Angew. Chem.* **2000**, *112*, 2857–2859; *Angew. Chem. Int. Ed.* **2000**, *39*, 2745–2747.

[12] X. C. Dong, F. C. Liu, Y. L. Zhao, *Acta Chim. Sin.* **1983**, *41*, 848–850.

[13] L. Yang, R. Yang, *Polyhedron* **1995**, *14*, 507–510; Y. Xing, X. Li, L. Yan, R. Yang, *Chem. J. Chin. Univ.* **1992**, *13*, 14–18; D. Zhou, Q. Li, C. Huang, G. Yao, S. Umetani, M. Matsui, L. Ying, A. Yu, X. Zhao, *Polyhedron* **1997**, *16*, 1381–1389.

[14] a) D. L. Kepert, *Prog. Inorg. Chem.* **1977**, *23*, 1–65; b) T. W. Hambley, D. L. Kepert, C. L. Raston, A. H. White, *Aust. J. Chem.* **1978**, *31*, 2635–2640.

[15] J. Xu, D. W. Whisenhunt, Jr., A. C. Veeck, L. C. Uhlir, K. N. Raymond. *Inorg. Chem.* **2003**, *42*, 2665–2674.

[16] P. Pyykkö, *Mol. Phys.* **2001**, *99*, 1617–1629.

[17] Crystallographic data: The X-ray diffraction data for $[\mathrm{Th_2}(\mathbf{L}^1)_4(\mathrm{dmf})_2]$ and $[\mathrm{Th_2}(\mathbf{L}^2)_4(\mathrm{dmf})_2]$ were collected on a Bruker SMART diffractometer by using graphite-monochromated $\mathrm{Mo_{K\alpha}}$ radiation. The structures were solved by using direct methods, expanded by Fourier techniques, and refined with the SHELX software package (G. M. Sheldrick, SHELX-97 Universität Göttingen, **1997**). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in idealized positions and induced in the structure factor calculations. CCDC-200541 and -200542 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Crystal data for $[\mathrm{Th_2}(\mathbf{L}^1)_4(\mathrm{dmf})_2]\cdot 6\,\mathrm{DMF}\cdot 0.5\,\mathrm{H_2O}$: $\mathrm{Th_2C_{106}H_{102}N_{18}O_{18}}\cdot 6\,\mathrm{C_3H_7NO}\cdot 0.5\,\mathrm{H_2O}$, $M_r = 2827.70$, colorless crystal, crystal dimension $0.32\times 0.27\times 0.20\ \mathrm{mm^3}$, monoclinic, space group $P2(1)/c$ (#14), $a = 24.7142(3)$, $b = 14.9788(3)$, $c = 37.4021(8)$ Å, $\beta = 105.447(1)°$, $V = 13345.7(4)$ Å^3, $Z = 4$, $F(000) = 5724$, $\rho_{\mathrm{calcd}} = 1.406\ \mathrm{g\,cm^{-3}}$, $\mu\mathrm{Mo_{K\alpha}} = 2.301\ \mathrm{mm^{-1}}$, radiation λ $(\mathrm{Mo_{K\alpha}}) = 0.71073$ Å, $T = 181(2)$ K, 58075 reflections collected ($2\theta_{\max} = 51.26°$), of which 22237 unique ($R_{\mathrm{int}} = 0.0545$). Data/restrains/parameters of 22237/0/1481, $R_1 = 0.0487$ ($wR_2 = 0.1218$, $I > 2\sigma(I)$), $R_1 = 0.0698$ ($wR_2 = 0.1293$, all data), GOF = 1.005. Crystal data for $[\mathrm{Th_2}(\mathbf{L}^2)_4(\mathrm{dmf})_2]\cdot 0.5\,\mathrm{DMF}\cdot 1.5\,\mathrm{C_4H_{10}O}$: $\mathrm{Th_2C_{110}H_{110}N_{18}O_{18}}\cdot 0.5\,\mathrm{C_3H_7NO}\cdot 1.5\,\mathrm{C_4H_{10}O}$, $M_r = 2583.97$, colorless crystal, crystal dimension $0.12\times 0.05\times 0.04$, triclinic, space group $P\bar{1}$ (#2), $a = 18.0226(19)$, $b = 19.107(2)$, $c = 20.390(8)$ Å, $\alpha = 110.845(2)$, $\beta = 114.358(2)$, $\gamma = 90.431(2)°$, $V = 5879.0(11)$ Å^3, $Z = 2$, $F(000) = 2606$, $\rho_{\mathrm{calcd}} = 1.460\ \mathrm{g\,cm^{-3}}$, $\mu\mathrm{Mo_{K\alpha}} = 2.301\ \mathrm{mm^{-1}}$, radiation λ $(\mathrm{Mo_{K\alpha}}) = 0.71073$ Å, $\mathrm{Mo_{K\alpha}}$, $T = 179(2)$ K, 18500 reflections collected ($2\theta_{\max} = 49.46°$), of which 12701 unique ($R = 0.0504$), data/restrains/parameters of 12701/0/1392. $R_1 = 0.0528$ ($I > 2\sigma(I)$), $wR_2 = 0.1195$, $R_1 = 0.0920$ ($wR_2 = 0.11368$, all data), GOF = 0.968.

[18] J. Xu, E. Radkov, M. Ziegler, K. N. Raymond, *Inorg. Chem.* **2000**, *39*, 4156–4164.

[19] G. D. Jarvinen, A. J. Zozulin, E. M. Larson, R. R. Ryan, *Acta Crystallogr. Sect. C* **1991**, *47*, 262–263.