Lord of the Rings: An Octameric Lanthanum Pyrazolonate Cluster**

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A continuing project in our laboratory has been the development of chelating agents for the lanthanide and actinide ions.[1] The special spectroscopic and magnetic properties of lanthanide complexes have prompted their use as luminescent probes, NMR shift agents, and as magnetic resonance imaging (MRI) agents.[2, 3] These applications rely on the precise control of the structural and electronic features of the metal coordination site(s).

The incorporation of trivalent lanthanide ions into self-assembling molecular architectures is currently also of great interest in supramolecular chemistry.[4] However, the trivalent lanthanide ions generally display variable and high (8, 9, or more) coordination numbers and the energy difference between the various coordination geometries is small; therefore they show low stereochemical preferences.[5] These factors make the rational design for the construction of supramolecular lanthanide complexes quite challenging. A better control of the coordination environment can be achieved through the use of highly predisposed ligands.[4a,b] These lead to a host of interesting and successful approaches but generally they also lead to enormously increased synthetic challenges.

Supramolecular helical species incorporating lanthanide ions were first reported in 1992 and have subsequently been prepared.[4c–g] A series of poly-*N* donor ligands of the 2,6-bisbenzimidazol-2-yl-pyridines has been studied in depth by the groups of Bünzli, Piguet, and Williams. The appeal of the helicate approach towards the preparation of well-defined coordination geometries lies in the fact that relatively simple ligands may be used. Given the right conditions, they will self-assemble into a large and predetermined structure. This process is crucially dependent on the geometry intrinsic to the particular metal–ligand interaction.

Bidentate 4-acyl-3-methyl-1-phenyl-2-pyrazolin-5-ones are β-diketonate chelators which were first synthesized at the turn of the last century.[6] Their complexing abilities, especially towards lanthanide and actinide ions, have also been long recognized and they are widely used for the separation of trace metals.[7] However it was not until 1983 that the tetradentate 4-acyl-2-pyrazolin-5-one ligands were synthesized and their coordination chemistry with lanthanide ions studied.[8a] These ligands form dinuclear lanthanide complexes which have interesting fluorescent properties.[8b–d] For example, the tetradentate ligand 3LIPYZL (1,5-Bis(1-phenyl-3-methyl-5-pyrazolone-4)-1,5-pentadione, H_2L) forms helical lanthanide(III) complexes with the stoichiometry $[Ln_2L_3]\cdot 4\,DMF$.[8b, 9] In contrast to the helical complexes formed with the six-coordinate d-block metal ions, the three tetradentate ligands can not saturate all the coordination sites of the two eight-coordinate lanthanide metal ions. Two solvent molecules fill the coordiation sites of each lanthanide ion. These structures reveal that lanthanide ions may form highly symmetric clusters with relatively simple 4-acyl-2-pyrazolin-5-one ligands, and leave some coordination vacancies for the solvent molecules to occupy. This is the guideline of our design of pyrazolonate-based lanthanide clusters.

Following the principles developed by our research group for the design of coordination clusters,[10] a tris-bidentate 4-acyl-2-pyrazolin-5-one ligand 4-(1,3,5-benzenetricarbonyl)-tris(3-methyl-1-phenyl-2-pyrazolin-5-one) (H_3L^1) was designed and synthesized. This rigid threefold-symmetric ligand forms a unique supramolecular three-dimensional ring architecture with first- and second-row transition metal ions such as Ga^{III},[11] V^{III}, Fe^{III}, and In^{III}.[12] These complexes have $[M_6L^1_6]$ architecture, which leads to three distinct environments for the three identical pyrazolone components of the ligand. The signals in the ^1H and ^{13}C NMR spectra of the Ga^{III} and In^{III} complexes show a characteristic triple splitting.[11, 12]

Based on the formation of these $[M_6L^1_6]$ three-dimensional ring structures it was reasoned that discrete supramolecular species might form with lanthanide ions, since the ligands do not necessarily have to saturate all of the coordination sites of the lanthanide ions. Indeed when the rigid threefold ligand H_3L^1 and lanthanum acetylacetonate $[La(acac)_3]$ were heated in DMSO, a high-yielding, self-assembly of a single species was observed (Scheme 1). The ^1H NMR spectra showed the characteristic triple splitting mode in the aliphatic as well as the aromatic regions (Figure 1). Similar phenomena were previously observed in $[M_6L^1_6]$ systems, which suggests that the lanthanum atoms may be located in similar coordination environments, and that the lanthanum complex may also have a three-dimensional ring structure. An X-ray crystallographic analysis[13] unambiguously revealed this complex to have a unique square-antiprismatic, three-dimensional ring structure $[La_8L^1_8]$ with idealized D_{4d} symmetry (Figure 2). Eight lanthanum atoms occupy the eight vertices of the polyhedron, while each ligand occupies one of the eight trianglar faces. Each lanthanum atom is coordinated by three ligands and each ligand coordinates to three lanthanum ions (Scheme 1). In this cluster nine-coordinate lanthanum atoms are linked by six-coordinate chelate ligands; this is a good example of coordination number residuum cluster formation. The residual coordination sites of the lanthanum ions are occupied by solvent molecules, some of which point into the cavity of the ring, as shown in Figure 2.

The coordinated DMSO solvent molecules can be easily replaced by other molecular donors such as alcohols, terpyridine, etc. In fact, when the complex that freshly precipitated from a DMSO solution was washed with methanol the complex dissolved and then re-precipitated. A batch of the

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Supporting information for this article is available on the WWW under http://www.wiley-vch.de/home/angewandte/ or from the author.

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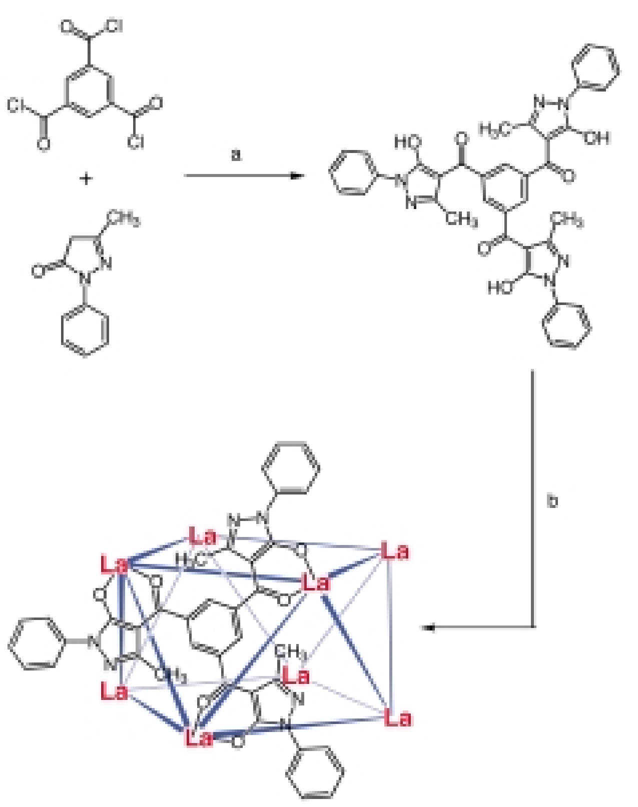

Scheme 1. Synthesis of the octomeric Lanthanide cluster $[La_8L^1_8]$. a) CaO/dioxane; b) [La(acac)$_3$]/DMSO, 100 °C, yield 81 %. The coordinated DMSO molecules are omitted for clarity.

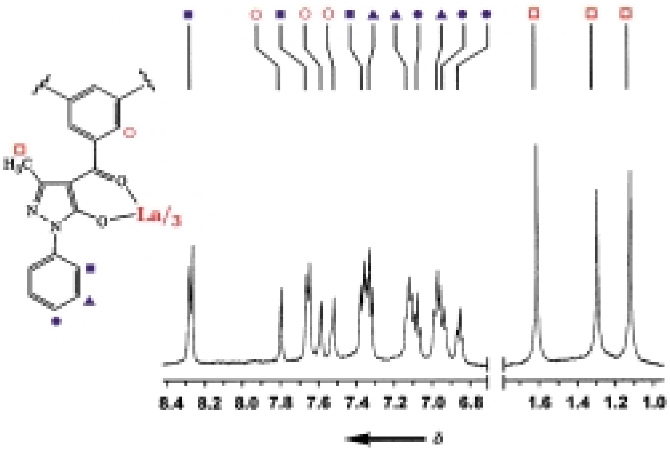

Figure 1. ^{1}H NMR spectrum of $[La_8L^1_8]$ in [D$_6$]DMSO. Only one of the three chemically inequivalent 4-acyl-pyrazolone moeities of the C_3-symmetric ligand is shown in the structure.

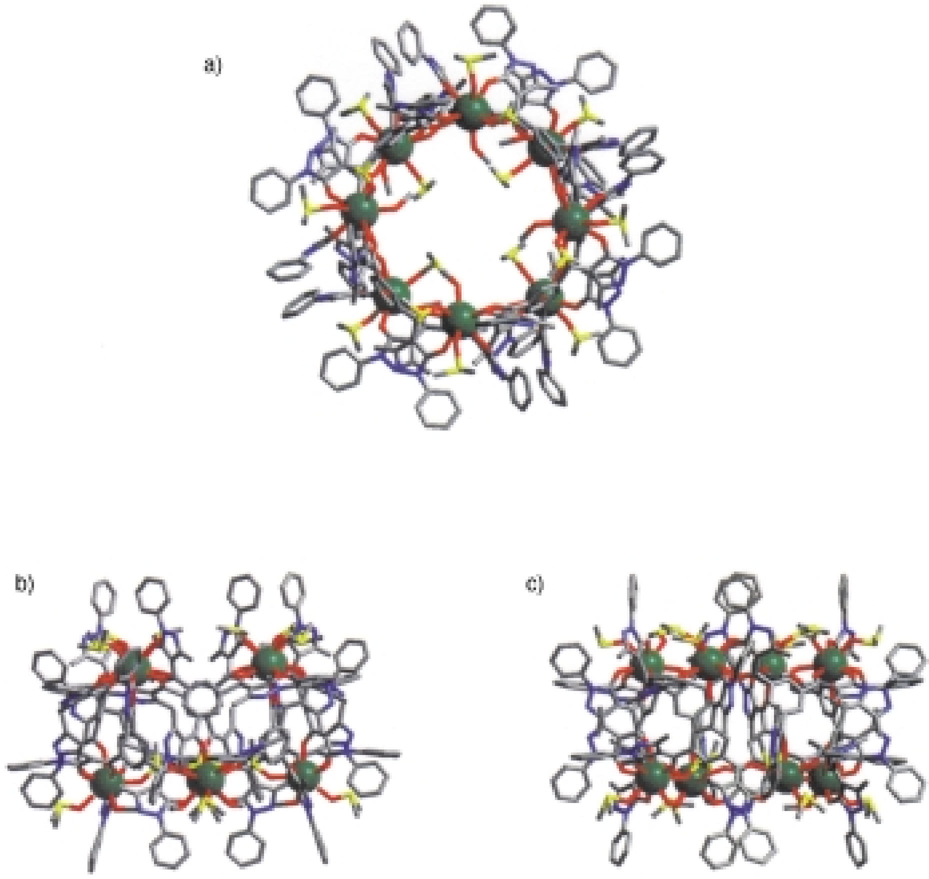

Figure 2. The X-ray crystal structure of $[La_8L^1_8]$, a) top view; b) and c) side views.

re-precipitated complex was dissolved in DMSO to grow crystals for X-ray structural analysis. Both MeOH and DMSO molecules were found in the structure.

The eight lanthanum atoms form a "regular" square-antiprism, both the upper and bottom sets form regular squares, and are offset by 45°. All of the distances between neighboring La atoms are equal within experimental error (10.1 and 10.3 Å). There are two lanthanum atoms (La1 and La2) in each asymmetric unit. Both lanthanum ions are nine-coordinate. The two possible ground-state geometries for nine-coordination polyhedra are the symmetrical tricapped trigonal prism with D_{3h} symmetry and the monocapped square antiprism with C_{4v} symmetry. The polyhedron of the La1 coordination sphere is best described as a slightly distorted monocapped square antiprism. The coordination polyhedron of La2 can be described as a distorted tricapped trigonal prism, in which the coordination polyhedron is distorted and has a lower symmetry (between the regular D_{3h} and C_{4v} structures).

In summary, a new lanthanum supramolecular architecture has been achieved in which nine-coordinate lanthanum centers are coordinated by three bidentate pyrazolone chelating units. These centers have been combined with a rigid C_3-symmetric ligand system to drive the formation of a square-antiprismatic cluster $[La_8L^1_8]$. This is the first example of a cyclic lanthanide cluster complex with a three-

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dimensional and highly symmetric ring structure, and is an extraordinary example of symmetry-driven cluster formation.

Experimental Section

General: All chemicals were used as received from Aldrich unless otherwise noted. The ^{1}H and ^{13}C NMR spectra were obtained on a Bruker DRX-500 spectrometer. Mass spectra and elemental analyses were performed at the MICRO-MASS Facility and the Elemental Analysis Facility, College of Chemistry, UC Berkeley, respectively.

H_3L^1: A suspension of 3-methyl-1-phenyl-2-pyrazolin-5-one (10.5 g, 0.06 mol) and calcium oxide (7.0 g, 0.12 mol) in dry dioxane (40 mL) was heated at 85 °C under nitrogen. A solution of 1,3,5-benzenetricarbonyl trichloride (5.0 g, 0.019 mol) in dry dioxane (10 mL) was added to this warm suspension over 1 min. The reaction mixture became a thick paste and the temperature increased immediately. The mixture was heated at reflux for 1 h, during which time the thick paste solidified. The dioxane solution was discarded and the solid was treated with 2 M HCl (250 mL). A beige solid was isolated by filtration, washed with cold water, and dried in vacuo at 60 °C overnight (yield 10.3 g, 82 %). Elemental analysis calcd for $C_{39}H_{30}N_6O_6 \cdot H_2O$ (%): C 67.23, H 4.62 N 12.06; found: C 67.01, H 4.61, N 12.06; ^{1}H NMR (500 MHz, [D$_6$]DMSO): $\delta = 2.32$ (s, 9 H), 7.29 (t, $J = 7.6$ Hz, 3 H), 7.43 (t, $J = 7.6$ Hz, 6 H), 7.65 (d, $J = 7.9$ Hz, 6 H), 8.30 (s, 3 H); ^{13}C NMR (500 MHz, [D$_6$]DMSO): $\delta = 14.21$, 104.35, 121.31, 121.41, 126.31, 129.03, 131.79, 136.66, 138.68, 150.77, 188.72; positive-ion FAB-MS: m/z: 679 [$H_3L^1 + H^+$].

$La_8L^1_8$: Lanthanum acetylacetonate hydrate (94 mg, 0.2 mmol) was added to a suspension of $H_3L^1 \cdot H_2O$ (154 mg, 0.22 mmol) in DMSO (10 mL). The reaction mixture was heated with stirring under nitrogen at 100 °C for 16 h. Upon cooling the mixture down to room temperature, the yellow powdery solid precipitate was collected by filtration and dried in a vacuum oven at 80 °C overnight (170 mg, 81 %, 0.20 mmol). Elemental analysis calcd for $La_8C_{360}H_{360}N_{48}O_{72}S_{24}$ ([$La_8L^1_8(DMSO)_{24}$]) (%): C 51.53, H 4.32, N 8.01; found: C 51.50, H 4.21, N 8.39; ^{1}H NMR (500 MHz, [D$_6$]DMSO): $\delta = 1.12$ (s, 3 H), 1.30 (s, 3 H), 1.61 (s, 3 H), 6.86 (t, $J = 7.4$ Hz, 1 H), 6.94 (t, $J = 7.4$ Hz, 1 H), 6.98 (t, $J = 8.0$ Hz, 2 H), 7.08 (t, $J = 7.8$ Hz, 1 H), 7.11 (t, $J = 7.6$ Hz, 2 H), 7.34 (t, $J = 7.8$ Hz, 2 H), 7.37 (d, $J = 8.0$ Hz, 2 H), 7.52 (s, 1 H), 7.59 (s, 1 H), 7.66 (d, $J = 7.9$ Hz, 2 H), 7.80 (s, 1 H), 8.28 (d, $J = 8.0$ Hz, 2 H); positive-ion FAB-MS: m/z: 6518 [$La_8L^1_8 + H^+$]; exact mass calcd for $La_8C_{312}H_{316}N_{48}O_{48}$: 6513.57.

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[1] a) J. Xu, S. J. Franklin, D. W. Whisenhunt, Jr., K. N. Raymond, *J. Am. Chem. Soc.* **1995**, *117*, 7245; b) J. Xu, P. W. Durbin, B. Kullgren, K. N. Raymond, *J. Med. Chem.* **1995**, *38*, 2606; c) S. J. Franklin, K. N. Raymond, *Inorg. Chem.* **1994**, *33*, 5794.

[2] a) J.-C. G. Bünzli in *Lanthanide Probes in Life, Chemical and Earth Sciences*, Elsevier, Amsterdam, **1989**, chap. 7; b) P. G. Sammes, G. Yahioglu, *Nat. Prod. Rep.* **1996**, *13*, 1; c) P. Guerriero, S. Tamburini, P. A. Vigato, *Coord. Chem. Rev.* **1995**, *139*, 17.

[3] R. B. Lauffer in *MRI Clinical Magnetic Resonance Imaging, Vol. 1*, 2nd ed., W. B. Sauders Co., Philadelphia, **1996**, chap. 5.

[4] a) J.-M. Lehn, *Supramolecular Chemistry, Concepts and Perspectives*, VCH, Weinheim, **1995**; b) S. Petoud, J.-C. G. Bünzli, F. Renaud, C. Piguet, K. J. Schenk, G. Hopfgartner, *Inorg. Chem.* **1997**, *36*, 5750; c) G. Bernardinelli, G. Hopfgartner, S. Petoud, O. Schaad, *J. Am. Chem. Soc.* **1996**, *118*, 6681; d) J.-C. G. Bünzli, P. Froidevaux, C. Piguet, *New J. Chem.* **1995**, *19*, 661; e) N. Sabbatini, M. Guardigli, J.-M. Lehn, *Coord. Chem Rev.* **1993**, *123*, 201; f) G. Bernardinelli, C. Piguet, A. F. Williams, *Angew. Chem.* **1992**, *104*, 1626; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1622; g) C. Piguet, G. Bernardinelli, G. Hopfgartner, *Chem. Rev.* **1997**, *97*, 2005.

[5] a) D. Kepert, *Inorganic Stereochemistry*, Springer, Berlin, **1982**, chap. 2 and 12–16; b) J.-C. G. Bünzli in *Basic and Applied Aspects of Rare Earths*, Editional Complutense, Madrid, **1997**.

[6] a) F. Stoltz, *J. Prakt. Chem.* **1897**, *55*, 145; b) A. Michaelis, F. Engelhardt, *Chem. Ber.* **1908**, *41*, 2668; c) W. Wislicenus, H. Elvert, *Chem. Ber.* **1913**, *46*, 3395.

[7] a) B. S. Jensen, *Acta Chem. Scand.* **1959**, *13*, 1347; b) B. S. Jensen, *Acta Chem. Scand.* **1959**, *13*, 1668; c) L. Lakov, P. Vassileva, E. Gocheva, Z. Fresenius, *Anal. Chem.* **1995**, *351*, 583; d) M. O. C. Ogwuegbu, N. C. Oforka, *Hydrometallurgy* **1994**, *34*, 359; e) O. Todorova, P. Vassileva, L. Lakov, Z. Fresenius, *Anal. Chem.* **1993**, *346*, 943; f) P. K. Mohapatra, V. K. Manchanda, *Radiochim. Acta* **1992**, *57*, 25.

[8] a) X. C. Dong, F. C. Liu, Y. L. Zhao, *Acta Chim. Sin.* **1983**, *41*, 848; b) L. Yang, R. Yang, *Polyhedron* **1995**, *14*, 507; c) Y. Xing, X. Li, L. Yan, R. Yang, *Chem. J. Chin. Univ.* **1992**, *13*, 14; d) D. Zhou, Q. Li, C. Huang, G. Yao, S. Umetani, M. Matsui, L. Ying, A. Yu, X. Zhao, *Polyhedron* **1997**, *16*, 1381.

[9] J. Xu, S. Petoud, C. Brückner, K. N. Raymond, unpublished results.

[10] a) D. L. Caulder, K. N. Raymond, *J. Chem. Soc. Dalton Trans.* **1999**, 1185; b) D. L. Caulder, K. N. Raymond, *Acc. Chem. Res.* **1999**, 975; c) T. Beissel, R. E. Powers, K. N. Raymond, *Angew. Chem.* **1996**, *108*, 1166; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1084; d) C. Brückner, R. E. Powers, K. N. Raymond, *Angew. Chem.* **1998**, *110*, 1937; *Angew. Chem. Int. Ed.* **1998**, *37*, 1837; e) D. L. Caulder, R. E. Powers, T. N. Parac, K. N. Raymond, *Angew. Chem.* **1998**, *110*, 1940; *Angew. Chem. Int. Ed.* **1998**, *37*, 1840.

[11] D. Johnson, J. Xu, R. Saalfrank, K. N. Raymond, *Angew. Chem. Int. Ed.* **1999**, *111*, 3058; *Angew. Chem. Int. Ed.* **1999**, *38*, 2882.

[12] J. Xu, S. Petoud, D. Johnson, K. N. Raymond, unpublished results.

[13] Crystal data for $[La_8(C_{39}H_{37}N_6O_6)_8 \cdot 9.3\,CH_3OH \cdot 10.7\,DMSO \cdot 4\,H_2O]] \cdot 20\,CH_3OH \cdot 12\,H_2O \cdot x$ solvent: tetragonal, space group $P4/n$ (Nr. 85), $a = 31.5567(3)$, $b = 31.5567(3)$, $c = 28.8080(5)$ Å, $V = 28687.7(6)$ Å^3, $Z = 2$, $\rho_{calcd} = 0.993$ g cm^{-3}, $\mu = 0.681$ mm^{-1}, $T = -115$ °C, $F(000) = 17088$. Crystal size 0.30 × 0.20 × 0.12 mm^3. Data were collected using a Siemens SMART diffractometer equipped with a CCD area detector $2\theta_{max} = 40.36°$, ω scans, graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). Of the 79543 reflections collected, 13351 were unique ($R_{int} = 0.1686$). The structure was solved by direct methods (SHELXL-97) and refined against F^2. Data were corrected for Lorentz and polarization effects. An empirical absorption correction was applied using SADABS (ellipsoidal model, $T_{max} = 0.900$, $T_{min} = O.730$). $R_1 = 0.1274$, $wR_2 = 0.2428$, $GOF = 1.380$ for 6072 reflections $F_o > 4\sigma(F_o)$ (6072 Friedel unique data, 838 parameters, 48 restraints, $3.66° < 2\theta < 40.36°$); and for all 13351 data $wR_2 = 0.2990$, $GOF = 1.378$. Max/min residual density $+0.648/-0.456$ e Å^{-3}. The low density of the structure probably reflects the presence of additional solvent molecules. Unfortunately we were unable to locate these, as a result of the low quality of the crystal data. Details of the disorder in the structure are obtained in the Supporting Information. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-141567. Copies of the data can be obtained free of charge upon application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).