173 (58) $[C_6H_{12}B_3N_4]^+$, 93 (90) $[C_3H_7B_2N_2]^+$; ^{1}H NMR (200 MHz, CD_2Cl_2): $\delta = 6.95$ (s, 2H, 4,5-H), 7.56 (s, 1H, 2-H); ^{13}C NMR (50 MHz, CD_2Cl_2): $\delta =$ 124.6 (s, C-4,5), 140.0 (s, C-2); ^{11}B NMR (64 MHz, CD_2Cl_2): $\delta = -9.5$ (s).

Tetrameric 1-imidazolyldimethylborane **4a**: The reaction was analogous to that of **3a**, **b**, but with CH_2Cl_2 instead of THF. Yield: 97% (contains 5% **4b**).

Tetrameric 1-(4,5-dimethylimidazolyl)borane **5a**: A BH_2Cl solution (40 mL of a 0.45 M solution in THF) was added dropwise to a stirred solution of **1b** (3.02 g, 17.9 mmol) in THF (150 mL) over 4 h at 0°C. The workup procedure was analogous to that of **3a**, **b** and gave colorless **5a** (1.65 g, 85%). EI-MS: m/z (%): 431 (55) $[M_4 - H]^+$, 337 (8) $[C_{15}H_{29}B_4N_6]^+$, 229 (60) $[C_{10}H_{20}B_3N_4]^+$, 216 (28) $[M_2]^+$, 203 (12) $[C_{10}H_{16}BN_4]^+$, 121 (100) $[C_5H_{11}B_2N_2]^+$, 108 (29) $[M]^+$; ^{1}H NMR (200 MHz, CD_2Cl_2): $\delta = 2.12$ (s, 6H, CH_3), 6.64 (s, 1H, 2-H); ^{13}C NMR (50 MHz, CD_2Cl_2): $\delta = 8.2$ (s, CH_3), 128.1 (s, C-4,5), 135.3 (s, C-2); ^{11}B NMR (64 MHz, CD_2Cl_2): $\delta = -11.8$ (s, br.).

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[3] Structural data of **3b**: monoclinic $P2_1/a$, $a = 18.315(9)$, $b = 16.547(8)$, $c = 20.456(10)$ Å, $\beta = 115.84(2)°$, $V = 5580(5)$ Å^3, $Z = 8$. A total of 7769 independent reflections (4227 observed, $I > 2\sigma(I)$), the measurement was carried out on a four-circle diffractometer ($Mo_{K\alpha}$ radiation, ω scan, $T = -60$°C) $R1 = 0.0842$, $wR2 = 0.2150$. Structural data of **5a**: monoclinic $P2_1/c$, $a = 12.5847(2)$, $b = 17.7859(3)$, $c = 11.4299(2)$ Å, $\beta = 106.3090(10)°$, $V = 2455.41(7)$ Å^3, $Z = 4$. A total of 5999 independent reflections (4691 observed, $I > 2\sigma(I)$), $R1 = 0.0552$, $wR2 = 0.1254$. The measurement was carried out on a Bruker AXS diffractometer ($Mo_{K\alpha}$ radiation, ω scan, $T = -100$°C). The structures were solved with direct methods (SHELXS86) and refined with all measured reflections against F^2 (SHELXL97).[8] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-133110 (**3b**) and CCDC-133111 (**5a**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Nitrophenolate as a Building Block for Lanthanide Chains and Clusters**

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Inorganic clusters continue to attract considerable attention because they represent the bridge linking molecular and solid state chemistry and because they are useful tools for understanding the size-dependent physical properties of electronic material.[1] While the cluster chemistry of the transition metals is now firmly established and huge clusters have been isolated—especially clusters of molybdenum,[2] copper,[3] and silver[4]—the analogous chemistry of the lanthanides is virtually undeveloped.[5] Whereas systematic studies on the lanthanide clusters of sulfur, selenium, and tellurium have recently been reported,[6] most of the lanthanide–oxygen clusters have been obtained by unexpected synthetic routes such as the decomposition of ether solvents,[7] the decomposition of grease,[8] or the reaction with traces of water in the mixture.[9] While we were preparing this paper, a systematic synthesis of pentadecanuclear lanthanide–tyrosine clusters from water was discovered by Zheng et al.[10]

We report here on the systematic preparation of lanthanide–oxygen clusters by partial hydrolysis of a water-sensitive reaction mixture. To reach this synthetic goal we were most interested in using a ligand which features different coordination modes. During our investigations it turned out that this is ideally achieved by using *o*-nitrophenolate. Transmetalation of potassium *o*-nitrophenolate with anhydrous yttrium or lutetium trichloride in THF with rigorous exclusion of air followed by crystallization from THF/pentane (1/4) leads to infinite chains of **1a** (Ln = Y) and **1b** (Ln = Lu). The

$[(THF)_4\{K(o\text{-}O_2NC_6H_4O)_4Ln\}_4]_n$ **1**

new complexes have been characterized by standard spectroscopic techniques, and the solid-state structures of **1a** and **1b** (Figure 1a) were established by single-crystal X-ray diffraction.[11] Compounds **1a** and **1b** are isostructural. Each lanthanide ion of **1** is surrounded by four *o*-nitrophenolate anions which act as bidentate ligands. Thus, each lanthanide ion is eightfold coordinated. Nevertheless, two different coordination modes of the *o*-nitrophenolate are realized in **1**; the nitro group may either point to the left side or to the right side of the chain. Thus, the dissimilarities in the coordination spheres of the lanthanide ions in **1** is caused by different orientations of the ligands around the metal center. The Ln–O bond lengths for Ln–OR are: 221.1(8)–231.8(9) (**1a**) and 219.5(12)–232.4(11) pm (**1b**); and for Ln–ONO are: 231.5(8)–249.7(8) (**1a**) and 234.7(11)–250.4(9) pm (**1b**). The potassium cations are located in between the

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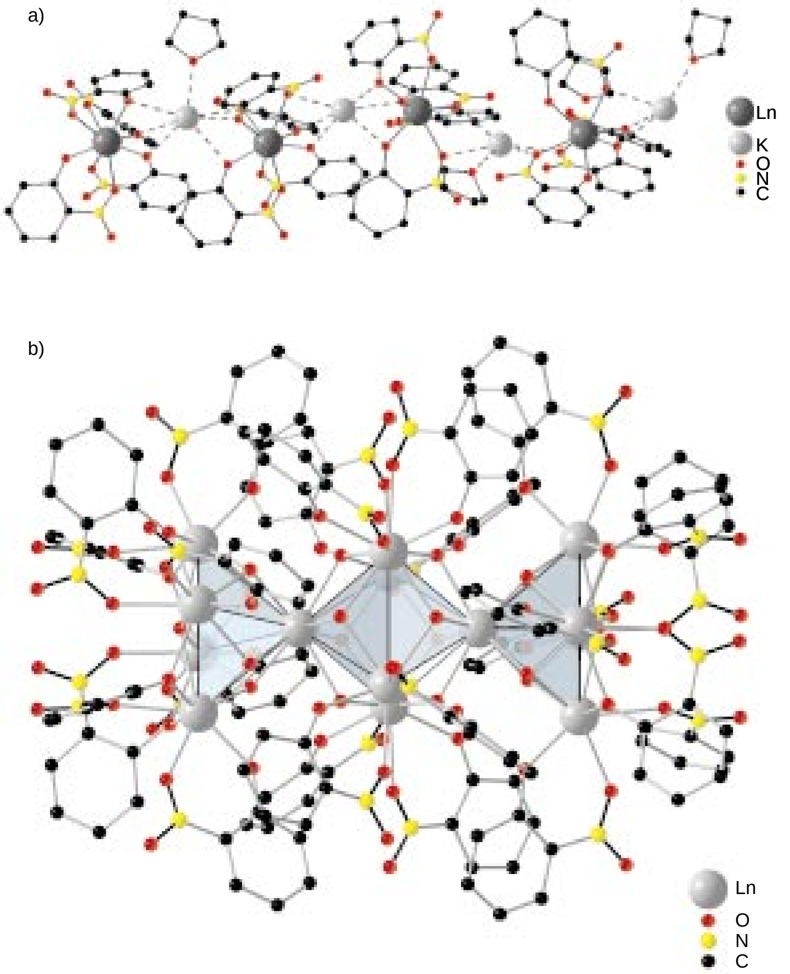

Figure 1. a) Solid-state structure of **1** (Ln = Y or Lu). One unit from an infinite chain is shown with hydrogen atoms omitted for clarity; b) solid-state structure of **2** (Ln = Er or Yb) with hydrogen atoms omitted for clarity.

$[(o\text{-}O_2NC_6H_4O)_4Ln]^-$ anions. Each potassium ion is coordinated by four to six nitro groups.[12] Additionally, one equivalent of THF is coordinated to three of the four potassium cations; the fourth equivalent of THF does not coordinate to a metal ion.

When the above reaction conditions were used with anhydrous erbium or ytterbium trichloride and the crystallization was performed in the presence of air, tetradecanuclear clusters of **2a** (Ln = Er) or **2b** (Ln = Yb) were obtained as orange crystals (Figure 1 b). For both compounds the solid-state structures were established by single-crystal X-ray diffraction.[13] We believe they are the largest lanthanide structures known,[5] besides **3**[14] and **4**.[10]

$[Ln_{14}(o\text{-}O_2NC_6H_4O)_{24}(\mu_4\text{-}OH)_2(\mu_3\text{-}OH)_{16}]$ **2**

$[Y_{14}(\mu_4\text{-}O)_2(\mu_3\text{-}Cl)_2(\mu\text{-}Cl)_8(\mu_3\text{-}OtBu)_4(\mu\text{-}OtBu)_{14}(OtBu)_{10}(THF)_4]$ **3**

$[Eu_{15}(Cl)(\mu_3\text{-tyrosine})(\mu_3\text{-}OH)_{20}(\mu\text{-}H_2O)_5(OH)_{12}(H_2O)_8][ClO_4]_2$ **4**

Cluster **2** is a highly symmetrical molecule which features a crystallographic D_4 symmetry. The Ln_{14} core of **2** can be described as a chain of three corner-sharing Ln octahedra, with a corner missing from the two outer octahedra (Figure 1 b). The octahedra are twisted at 45° to each other. Each triangular face of these octahedra is capped by one μ_3-OH group, which means the two corner-sharing Ln ions are each surrounded by eight μ_3-OH groups in a square-antiprismatic fashion. In contrast to the well-known $[M_6X_8]^{n+}$ clusters such as $[Mo_6Cl_8]^{4+}$[15] no metal–metal bonding is observed in **2**. One oxygen atom is attached to the four lanthanide ions on the cut-off face of the outer octahedra. These μ_4-bonded oxygen atoms are shifted 52 pm out of the Ln_4 square plane. The Ln–O bond distances to these oxygen atoms are: 250.9(3) (**2a**) and 247.5(3) pm (**2b**).[16]. Each of the twelve Ln ions which are non-corner-sharing is coordinated by two *o*-nitrophenolate ligands. The different coordination modes which are observed in **2** (Figure 1 b) demonstrate the flexibility of the *o*-nitrophenolate ligand. Although no structural investigations on lanthanide *o*-nitrophenols are known, there are a number of publications dealing with lanthanide picrates.[17] Most of these compounds are mono- or dinuclear complexes which were prepared in water.

Whereas most lanthanide oxide clusters seem to be formed by a partial hydrolysis of the reaction mixture and the syntheses are hard to reproduce, we were able to synthesize **2** several times, even when using different batches of solvent and starting material.[18] Both **1** and **2** could only be obtained by the reaction of potassium *o*-nitrophenolate with the chlorides of the heavier lanthanides or yttrium. No reaction was observed upon mixing potassium *o*-nitrophenolate and $LaCl_3$ in THF. Since $LaCl_3$ is less soluble in THF than the heavier lanthanide trichlorides, this observation is not surprising.

In summary, the reaction of potassium *o*-nitrophenolate with anhydrous yttrium and some of the lanthanide trichlorides gives unusual products. In the absence of air infinite chains were obtained, whereas crystallization in air leads to tetradecanuclear lanthanide clusters. To the best of our knowledge the setup of these clusters is unique in coordination chemistry.

Experimental Section

1 and **2**: Under a nitrogen atmosphere THF (25 mL) was added to a mixture of $LnCl_3$ (2.0 mmol) and potassium *o*-nitrophenolate (1.063 g, 6 mmol) at room temperature. The mixture was stirred for 16 h at room temperature and then the solution was filtered and concentrated.

1: Pentane was layered on top of the recrystallization solution (THF/pentane, 1/4). Orange crystals were obtained after one day. **1a**: Yield 410 mg (37 %); ^1H NMR ([D$_8$]THF, 250 MHz, 25 °C): $\delta = 1.72-1.79$ (m; THF), 3.57–3.66 (m; THF), 6.36 (t, 1 H; Ph), 6.66 (d, 1 H; Ph), 7.15 (t, 1 H; Ph), 7.73 (d, 1 H; Ph); IR (KBr disk): $\tilde{\nu} = 1598$ (s; C=C), 1537 (s; C–NO$_2$), 1485 (s), 1426 (s), 1319 (s), 1252 (s; C–O), 1140 (s), 1081 (s), 1019 (m), 745 (s) cm^{-1}; elemental analysis calcd. for $C_{112}H_{96}K_4N_{16}O_{52}Y_4$ (3010.09): C 44.69, H 3.21, N 7.45; found: C 44.22, H 3.55, N 7.69. **1b**: Yield 344 mg (28 %); ^1H NMR ([D$_8$]THF, 250 MHz, 25 °C): $\delta = 1.72-1.79$ (m; THF), 3.57–3.66 (m; THF), 6.49 (t, 1H; Ph), 6.70 (d, 1H; Ph), 7.32 (t, 1H; Ph), 7.89 (d, 1H; Ph); IR (KBr disk): $\tilde{\nu} = 1599$ (s; C=C), 1540 (s; $C{-}NO_2$), 1502 (s), 1427 (s), 1324 (s), 1255 (s; C–O), 1135 (s), 1083 (s), 1018 (s), 799 (s), 746 (s) cm^{-1}; elemental analysis calcd. for $C_{112}H_{96}K_4Lu_4N_{16}O_{52}$ (3354.33): C 40.10, H 2.88, N 6.68; found: C 39.22, H 2.98, N 6.11.

2: In the presence of air hexane was layered on top of the recrystallization solution (THF/hexane, 1/4), and then the reaction vessel was closed. Orange crystals were obtained after 12 h. **2a**: Yield 110 mg (12%); IR (KBr disk): $\tilde{\nu} = 3526$ (w; OH), 3106 (w), 1604 (vs; C=C), 1541 (m; $C{-}NO_2$), 1503 (vs), 1463 (s), 1324 (vs), 1249 (vs; C–O), 1137 (vs), 1083 (s), 799 (s) 745 (s) cm^{-1}; elemental analysis calcd. for $C_{176}H_{178}Er_{14}N_{24}O_{98}$ (6539.06): C 32.72, H 2.39, N 5.24; found: C 32.85, H 2.99, N 5.98. **2b**: Yield 130 mg (14%); IR (KBr disk): 3520 (w; OH), 3100 (w),1604 (vs; C=C), 1557 (s; $C{-}NO_2$), 1541 (s), 1505 (vs), 1468 (s), 1324 (vs), 1258 (vs; C–O), 1136 (vs), 1086 (vs), 801 (s) 744 (s) cm^{-1}; elemental analysis calcd. for $C_{176}H_{178}N_{24}O_{98}Yb_{14}$ (6619.98): C 31.93, H 2.71, N 5.08; found: C 31.87, H 2.64, N 5.57.

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[11] Single-crystal X-ray diffraction data:[19] **1a** ($C_{112}H_{96}K_4N_{16}O_{52}Y_4$, $M_r = 3010.09$): space group $P\bar{1}$ (no. 2), $a = 1213.0(2)$, $b = 2063.2(4)$, $c = 2597.4(5)$ pm, $\alpha = 102.96(3)$, $\beta = 94.34(3)$, $\gamma = 94.77(3)^\circ$ at 203 K, $Z = 2$, $V = 6283(2)\ 10^6\,pm^3$, $\rho = 1.591\ g\,cm^{-3}$, $2\theta_{max} = 48^\circ$, 36557 reflections collected, 18671 independent reflections ($R_{int} = 0.1304$), 8511 refined reflections with $I > 2\sigma(I)$ to $R^1 = 0.0859$ and $wR^2 = 0.1853$. **1b** ($C_{112}H_{96}K_4Lu_4N_{16}O_{52}$, $M_r = 3354.33$): space group $P\bar{1}$ (no. 2), $a = 1210.6(2)$, $b = 2037.2(4)$, $c = 2591.9(5)$ pm, $\alpha = 103.00(3)$, $\beta = 93.91(3)$, $\gamma = 94.92(3)^\circ$ at 203 K, $Z = 2$, $V = 6180(2)\ 10^6\,pm^3$, $\rho = 1.802\ g\,cm^{-3}$, $2\theta_{max} = 50^\circ$, 42925 reflections collected, 20437 independent reflections ($R_{int} = 0.1010$), 16256 refined reflections with $I > 2\sigma(I)$ to $R_1 = 0.0774$ and $wR_2 = 0.2224$.

[12] We consider a K–O interaction to be a coordinating interaction if the K–O distance is significantly shorter than 300 pm.

[13] Single crystal X-ray diffraction data:[19] **2a** × 8THF ($C_{176}H_{178}Er_{14}N_{24}O_{98}$, $M_r = 6539.06$): space group $P4/nnc$ (no. 126), $a = 1927.0(9)$, $c = 3381.0(7)$ pm at 203 K, $Z = 2$, $V = 12555(4)\ 10^6\,pm^3$, $\rho = 1.730\ g\,cm^{-3}$, $2\theta_{max} = 45^\circ$, 19412 reflections collected, 4059 independent reflections ($R_{int} = 0.0744$), 2940 refined reflections with $I > 2\sigma(I)$ to $R_1 = 0.0481$ and $wR_2 = 0.1477$. **2b** × 8THF ($C_{176}H_{178}N_{24}O_{98}Yb_{14}$, $M_r = 6619.98$): space group $P4/nnc$ (no. 126), $a = 1919.7(3)$, $c = 3465.6(7)$ pm at 203 K, $Z = 2$, $V = 12403(4)\ 10^6\,pm^3$, $\rho = 1.773\ g\,cm^{-3}$, $2\theta_{max} = 45^\circ$, 34864 reflections collected, 4040 independent reflections ($R_{int} = 0.0680$), 3239 refined reflections with $I > 2\sigma(I)$ to $R_1 = 0.0506$ and $wR_2 = 0.1524$. In both structures the H atoms could not be refined.

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[18] Compound **2a** was made four times and **2b** twice. The lattice constants of the obtained crystals were determined by single-crystal X-ray diffraction each time and found to be the same.

[19] X-ray structure analyses: General: All data sets were collected by STOE-IPDS. The structure was solved by Patterson methods (SHELXS-86 and SHELXL-93) and refined by full-matrix least-square techniques. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC-134394 (**1a**), -134395 (**1b**), -136363 (**2a**), and -134397 (**2b**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; email: deposit@ccdc.cam.ac.uk).

Molecular Recognition of Carbohydrates by Artificial Polypyridine and Polypyrimidine Receptors**

Monika Mazik,* Heinz Bandmann, and Willi Sicking

The molecular recognition of carbohydrates is one of the challenging goals of supramolecular chemistry.[1a)] This is due to the three-dimensional complexity of sugar structures and to the key roles which carbohydrates play in a wide range of biological processes.[1b)] The analysis of the X-ray crystallographic structures of sugar–protein complexes reveals that hydrogen bonds between hydroxy groups as well as between ring oxygens of the sugar molecule and polar residues of the protein are the main factors in conferring specificity and affinity to protein–carbohydrate interactions.[2] Furthermore, stacking of sugar CH moieties with aromatic amino acid side chains, such as the indole and phenol rings of Trp and Tyr, respectively, modulates the stability of protein–carbohydrate complexes.

Mimicking these binding strategies may lead to effective, artificial systems as a key for developing new types of biorelevant materials. Systematic biomimetic studies with synthetic receptors should lead to better understanding of carbohydrate recognition in biological processes. Despite intense current interest in the development of artificial carbohydrate receptors,[3–5] only a few effective hydrogen-bonding host molecules can be found in the literature for sugars in organic solvents. The described carbohydrate receptors mostly possess macrocyclic structures, are accessible only by multistep syntheses, and, although multidentate, are often essentially two-dimensional.[6]

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