Nitrophenolate as a Building Block for Lanthanide Chains, Layers, and Clusters

Markus R. Bürgstein,[†] Michael T. Gamer,[‡] and Peter W. Roesky*,[‡]

Contribution from the Forschungszentrum Karlsruhe GmbH, Institut für Technische Chemie, Chemisch-Physikalische Verfahren (ITC-CPV), Postfach 3640, 76021 Karlsruhe, Germany, and Institut für Chemie, Freie Universität Berlin, Fabeckstrasse 34-36, 14195 Berlin, Germany

Received November 14, 2003; E-mail: roesky@chemie.fu-berlin.de

Abstract: Potassium *o*-nitrophenolate (**1**) was reacted with various lanthanide trichlorides under different reaction conditions. By using the smaller lanthanides and working under rigorous exclusion of air, infinite chains of composition $[(THF)_4\{K(o\text{-}O_2N\text{-}C_6H_4\text{-}O)_4Ln\}_4]_n$ (Ln = Y (**2a**), Er (**2b**), Lu (**2c**)) were obtained. Using the same conditions but performing the crystallization under air, tetradecanuclear clusters of composition $H_{18}[Ln_{14}(\mu\text{-}\eta^2\text{-}o\text{-}O_2N\text{-}C_6H_4\text{-}O)_8(\eta^2\text{-}o\text{-}O_2N\text{-}C_6H_4\text{-}O)_{16}(\mu_4\text{-}O)_2(\mu_3\text{-}O)_{16}]$ (Ln = Dy (**3a**), Er (**3b**), Tm (**3c**), Yb (**3d**)) were isolated. Using larger center metals such as samarium, europium, and terbium and working under rigorous exclusion of air, infinite layers of composition $[[K_2(o\text{-}O_2N\text{-}C_6H_4\text{-}O)_5Tb]_n]$ (**4**) and $[[K_2(o\text{-}O_2N\text{-}C_6H_4\text{-}O)_5Ln)]_n$ (Ln = Sm (**5a**), Eu (**5b**)) were obtained. In **4** the layers have a closer packing than those in compound **5**. The closer packing is a result of the increased coordination number of the lanthanide metal and the potassium atoms. In contrast, the more open structures of **5** results in channels which are rectangular through the layers. All compounds reported including **1** have been investigated by single-crystal X-ray diffraction.

Introduction

The construction of coordination polymers has been a field of rapid growth in supramolecular and material chemistry due to the formation of fascinating structures and potential applications as new materials.[1] So far, most of the work reported in the literature has been focused on the coordination polymers of *d*-block transition metal elements.[2] Recently a few examples have appeared on lanthanide-based frameworks employing polydentate ligands such as sulfoxides,[3] carboxylates,[4] pyridones,[5] lactames,[6] and 4,4′-bipyridine-*N*,*N*′-dioxide.[7] The lanthanide ions generally display variable and high coordi-

nation numbers, and the energy between the various coordination numbers is small. Therefore, the use of lanthanide ions as nodes for the construction of coordination polymers is more difficult than their *d*-block metal analogues.[3a] Similar observations have been made for coordination oligomers (clusters). 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.[8] While the cluster chemistry of the *d*-block transition metals is now firmly established and huge clusters especially of molybdenum,[9] copper,[10] and silver[11] were isolated, the analogous chemistry of the lanthanides is virtually underdeveloped.[12,13]

    [†] Forschungszentrum Karlsruhe GmbH.
    [‡] Freie Universität Berlin.
 (1) (a) Moulton, B.; Zaworotko, M. J. *Chem. Rev.* **2001**, *101*, 1629−1658. (b) Eddaoudi, M.; Moler, D. B.; Li, H.; Chen, B.; Reineke, T. M.; O'Keeffe, M.; Yaghi, O. M. *Acc. Chem. Res.* **2001**, *34*, 319−330. (c) Yaghi, O. M.; Li, H.; Davis, C.; Richardson, D.; Groy, T. L. *Acc. Chem. Res.* **1998**, *31*, 474−484.
 (2) (a) Batten, S. R.; Robson, R. *Angew. Chem.* **1998**, *110*, 1558−1595; *Angew. Chem., Int. Ed.* **1998**, *37*, 1460−1494. (b) Blake, A. J.; Champness, N. R.; Hubberstey, P.; Li, W. S.; Schröder, M. *Coord. Chem. Rev.* **1999**, *183*, 117−138.
 (3) (a) Bu, X.-H.; Weng, W.; Chen, W.; Zhang, R.-H. *Inorg. Chem.* **2002**, *41*, 413−415. (b) Bu, X.-H.; Weng, W.; Du, M.; Chen, W.; Li, J.-R.; Zhang, R.-H.; Zhao, L.-J. *Inorg. Chem.* **2002**, *41*, 1007−1010. (c) Zhang, R.-H.; Ma, B.-Q.; Bu, X.-H.; Yao, X.-K. *Polyhedron* **1997**, *16*, 1123.
 (4) (a) Reineke, T. M.; Eddaoudi, M.; Moler, D.; O'Keeffe, M.; Yaghi, O. M. *J. Am. Chem. Soc.* **2000**, *122*, 4843−4844. (b) Lee, E.; Heo, J.; Kim, K. *Angew. Chem.* **2000**, *112*, 2811−2813; *Angew. Chem., Int. Ed.* **2000**, *39*, 2699−2701. (c) Mao, J. G.; Zhang, H. J.; Ni, J. Z.; Wang, S. B.; Mak, T. C. W. *Polyhedron* **1999**, *18*, 1519−1525. (d) Ma, L.; Evans, O. R.; Foxman, B. M.; Lin, W. *Inorg. Chem.* **1999**, *38*, 5837−5840. (e) Pan, L.; Huang, X.; Li, J.; Wu, Y.; Zheng, N. *Angew. Chem.* **2000**, *112*, 537−540; *Angew. Chem., Int. Ed.* **2000**, *39*, 527−530. (f) Reineke, T. M.; Eddaoudi, M.; O'Keeffe, M.; Yaghi, O. M. *Angew. Chem., Int. Ed.* **1999**, *38*, 2590−2594. (g) Reineke, T. M.; Eddaoudi, M.; Fehr, M.; Kelley, D.; Yaghi, O. M. *J. Am. Chem. Soc.* **1999**, *121*, 1651−1657.

 (5) (a) Goodgame, D. M. L.; Menzer, S.; Smith, A. M.; Williams, D. J. *Chem. Commun.* **1997**, 339−340. (b) Goodgame, D. M. L.; Hill, S. P. W.; Williams, D. J. *Inorg. Chim. Acta* **1998**, *272*, 131−140.
 (6) (a) Doyle, G. A.; Goodgame, D. M. L.; Hill, S. P. W.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1993**, 207−209. (b) Carrad, L. H.; Goodgame, D. M. L.; Hill, S. P. W.; Williams, D. J. *J. Chem. Soc., Chem. Dalton Trans.* **1993**, 1003−1008. (c) Goodgame, D. M. L.; Menzer, S.; Ross, A. T.; Williams, D. J. *Inorg. Chim. Acta* **1996**, *251*, 141−149.
 (7) (a) Long, D.-L.; Blake, A. J.; Champness, N. R.; Wilson, C.; Schröder, M. *J. Am. Chem. Soc.* **2001**, *123*, 3401−3402. (b) Long, D.-L.; Blake, A. J.; Champness, N. R.; Schröder, M. *Chem. Commun.* **2000**, 136−1370.
 (8) (a) *Clusters and Colloids. From Theory to Applications*; Schmid, G., Ed.; VCH: Weinheim, Germany, 1994. (b) *Physics and Chemistry of Metal Cluster Compounds*; de Jongh, L. J., Ed.; Kluwer: Dordrecht, The Netherlands, 1994.
 (9) Müller, A.; Krickmeyer, E.; Bögge, H.; Schmidtmann, M.; Peters, F. *Angew. Chem.* **1998**, *110*, 3567−3571; *Angew. Chem., Int. Ed.* **1998**, *37*, 3360−3363.
(10) Krautscheid, H.; Fenske, D.; Baum, G.; Semmelmann, M. *Angew. Chem.* **1993**, *105*, 1364−1367; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1303−1306.
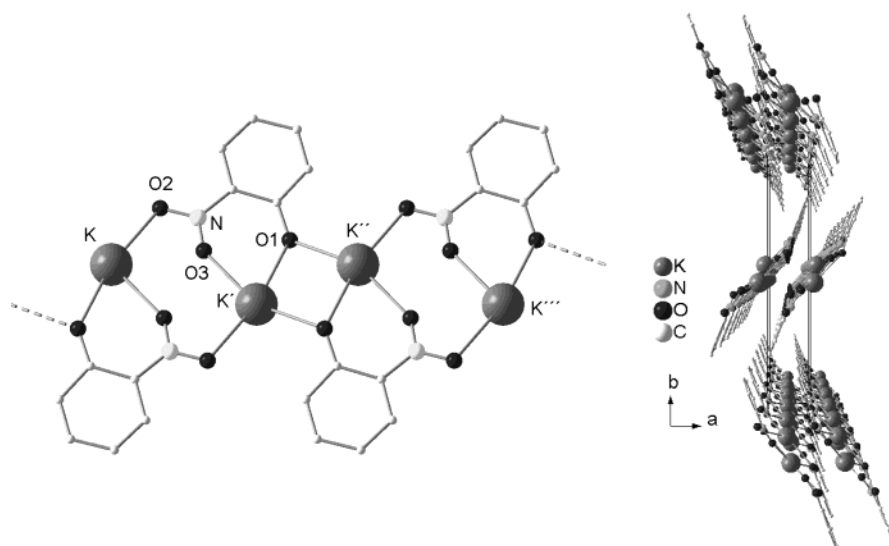
Figure 1. Left: Solid-state structure of **1** showing the atom labeling scheme, omitting hydrogen atoms. Shown are four units out of an infinite chain. Right: Solid-state structure of **1** along the *c*-axis. Selected bond lengths [Å] and angles [deg]: K—O2 2.851(2), K′—O1 2.827(1), K′—O3 2.680(1), K″—O1 2.827(1); N—O2—K 99.70(10), O1—K′—O3 58.33(4), K′—O1—K″ 72.56(3).

Recently, we communicated both lanthanide clusters and coordination polymers employing *o*-nitrophenolate as ligand.[14] Infinite chains of composition [(THF)$_4${K(o-O$_2$N-C$_6$H$_4$-O)$_4$-Ln}$_4$]$_n$ (Ln = Y, Lu) and tetradecanuclear oxo/hydroxo clusters of composition [Ln$_{14}$(o-O$_2$N-C$_6$H$_4$-O)$_{22}$(o-O$_2$N-C$_6$H$_4$-OH)$_2$-(μ_4-O)$_2$(μ_3-OH)$_{16}$] (Ln = Er, Yb) were obtained. Thus, it turned out that *o*-nitrophenolate is a ligand, which features different coordination modes and thus is able to stabilize different sorts of coordination polymers and oligomers.

In this contribution, we present now a full account of the reaction of potassium *o*-nitrophenolate with yttrium and nine different lanthanide trichlorides. Depending on the ion radius and the reaction conditions, either clusters, infinite chains, or infinite layers of different shape were obtained.

Results and Discussion

Ligand. To avoid the well-known problems of incorporation of lithium chloride into the coordination sphere of the lanthanide metals, we were initially interested in the synthesis of the potassium salt of the ligand.[15] Treatment of *o*-nitrophenole with *t*BuOK in boiling THF leads to the desired reagent potassium *o*-nitrophenolate (**1**) as red precipitate in almost quantitative yield (eq 1). The structure of **1** was confirmed by single-crystal X-ray diffraction in the solid-state (Figure 1, left). Data collection parameters are given in Table 1 in the Supporting Information. Compound **1** crystallizes in the space group *P*2$_1$/*n* in form of infinite double chains. These double chains are parallel to each other along the *a*-axis and form a zigzag setup along the *b*-axis (Figure 1, right). The nearby double chains are held together by K—O contacts, which are in the range of 3.0 Å. Each *o*-nitrophenolate unit binds to three potassium atoms via all oxygen atoms. Thus O2 is coordinated to the first
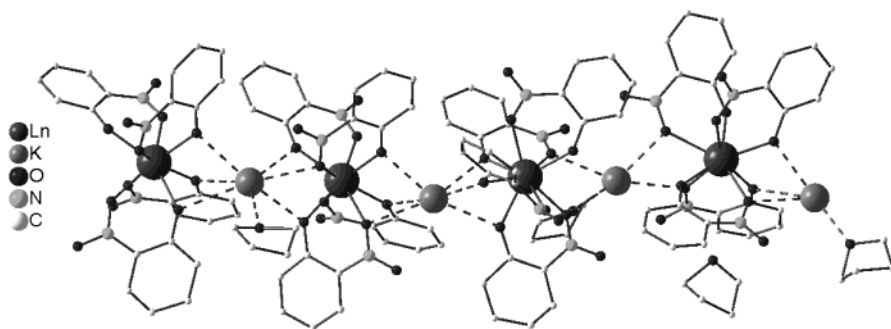
(11) Fenske, D.; Zhu, N.; Langetepe, T. *Angew. Chem.* **1998**, *110*, 2784−2788; *Angew. Chem., Int. Ed.* **1998**, *37*, 2640−2644.
(12) Anwander, R. *Angew. Chem.* **1998**, *110*, 619−622; *Angew. Chem., Int. Ed.* **1998**, *37*, 599−602.
(13) Zheng, Z. *Chem. Commun.* **2001**, 2521−2529.
(14) Bürgstein, M. R.; Roesky, P. W. *Angew. Chem.* **2000**, *112*, 559−562; *Angew. Chem., Int. Ed.* **2000**, *39*, 549−551.
(15) Edelmann, F. T. In *Comprehensive Organometallic Chemisty II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: Oxford, 1995.

potassium atom (K—O2 2.851(2) Å), O3 and O1 coordinate to the second potassium atom in a chelating fashion (K′—O1 2.827(1) Å, K′—O3 2.680(1) Å), and O1 forms a symmetric bridge between the second and the third potassium atom (K′—O1 and K″—O1 2.827(1) Å). The structure of **1** already indicates the flexible coordination behavior of *o*-nitrophenolate, which seems the requirement to form polymeric lanthanide complexes.
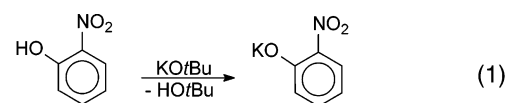
Infinite Chains. Transmetallation of **1** with anhydrous yttrium, erbium, and lutetium trichloride in THF under rigorous exclusion of air and subsequent crystallization from THF/*n*-pentane (1:4) led to infinite chains of composition [(THF)$_4$-{K(o-O$_2$N-C$_6$H$_4$-O)$_4$Ln}$_4$]$_n$ (Ln = Y (**2a**), Er (**2b**), Lu (**2c**)) (eq 2). The new complexes were characterized by standard spectroscopic techniques and the solid-state structures of **2a**−**2c** (Figure 2) were established by single-crystal X-ray diffraction. Compounds **2a**−**2c** are isostructural. The lanthanide ion of **2** is surrounded by four *o*-nitrophenolate anions which act as bidentate ligands. Thus, each lanthanide atom is 8-fold coordinated. Nevertheless, there are two different coordination modes of the *o*-nitrophenolate realized in **2**. The nitro group may either point to the left side or to the right side of the chain. Thus, the dissimilarity of the coordination sphere of the lanthanide atoms in **2** is based on different orientations of the ligands around the metal center. The Ln—O bond lengths range as follows for Ln—OR: **2a**, 2.211(8)−2.318(9) Å; **2b**, 2.211(5)−2.325(6) Å; **2c**, 2.188(12)−2.302(11) Å. For Ln—ONO they range as follows: **2a**, 2.321(10)−2.497(8) Å; **2b**, 2.296(6)−2.509(5) Å; **2c**, 2.276(12)−2.478(9) Å. Between the [(o-O$_2$N-C$_6$H$_4$-O)$_4$Ln]$^-$ anions the potassium cations are located. Each potassium atom is coordinated by four to six nitro groups.[16] Additionally, to three of the four potassium atoms one equivalent of THF is
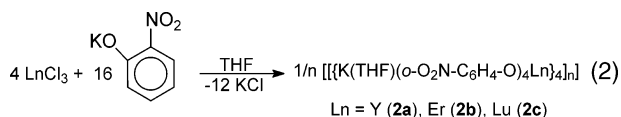
(16) We consider a K—O interaction as coordinating if the K—O distance is significantly shorter than 3.00 Å.
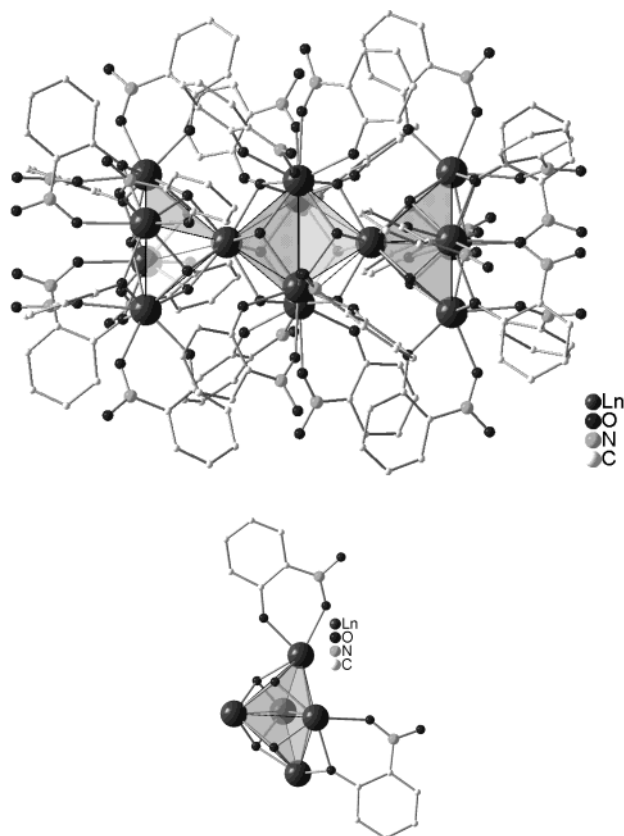
Figure 2. Solid-state structure of **2** showing the atom labeling scheme, omitting hydrogen atoms. Shown is one unit out of an infinite chain (Ln = Y, Er, Lu).

coordinated, whereas the fourth equivalent of THF does not coordinate to any metal atom.

Clusters. By using the same reaction conditions as for the synthesis of **2** but performing the crystallization under air, tetradecanuclear clusters of composition $H_{18}[Ln_{14}(\mu-\eta^2-o-O_2N-C_6H_4-O)_8(\eta^2-o-O_2N-C_6H_4-O)_{16}(\mu_4-O)_2(\mu_3-O)_{16}]$ (Ln = Dy (**3a**), Er (**3b**), Tm (**3c**), Yb (**3d**)) were obtained as orange crystals. For all compounds the solid-state structures were established by single-crystal X-ray diffraction (Figure 3).[17] Although the hydrogen atoms were not localized by single-crystal X-ray diffraction, we anticipate that all μ_3-O and μ_4-O atoms based on the IR data and the charge balance are OH groups. To the best of our knowledge, **3** is, besides $[Y_{14}(\mu_4-O)_2(\mu_3-Cl)_2(\mu-Cl)_8-(\mu_3-OtBu)_4(\mu-OtBu)_{14}(OtBu)_{10}(THF)_4]$[18] and $[Eu_{15}(Cl)(\mu_3-ty-rosine)(\mu_3-OH)_{20}(\mu-H_2O)_5(OH)_{12}(H_2O)_8][ClO_4]_2$[19] the largest lanthanide cluster known.[12] **3** is a highly symmetric molecule which features a crystallographic D_4 symmetry. The Ln_{14}-core of **3** can be described as a chain of three corner sharing Ln octahedra, in which one corner of the two outer octahedra is missing. The octahedra are 45° twisted to each other. Each triangular face of these octahedra is capped by one μ_3-O group. The two corner sharing Ln atoms are surrounded by eight μ_3-O groups in a square antiprismatic fashion. In the outer octahedra of **3**, one oxygen atom is encapsulated by four lanthanide atoms. Thus, the encapsulated outer oxygen atoms are μ_4-bonded. The μ_4-oxygen atoms are 0.529(1) (**3b**), 0.539(1) (**3c**), and 0.525(1) Å (**3d**) shifted out of the Ln_4 least-squares plane. The Ln–O bond distances to the Ln–μ_4-O oxygen atoms are 2.509(3) (**3b**), 2.504(3) (**3c**), and 2.475(3) Å (**3d**). Each of the twelve noncorner sharing Ln atoms is coordinated by two *o*-nitrophenolate ligands. The flexibility of the *o*-nitrophenolate is demonstrated by the different coordination modes of the ligand which are observed in **3**. Thus 16 pure chelating η^2-*o*-nitrophenolates and eight metal bridging $\mu-\eta^2$-*o*-nitrophenolates are observed. In both cases the *o*-nitrophenolate coordinates via oxygen atoms of the nitro and the phenoxy group onto the metal center. The diameter of **3** is about 2.06 nm.

Figure 3. Top: Solid-state structure of **3** showing the atom labeling scheme, omitting hydrogen atoms (Ln = Dy, Er, Tm, Yb). Bottom: Shown is a cutout of the structure indicating the two different coordination modes of the ligand.

As pointed out by Wang and Yan the structure of **3** is based on a common structural motive in lanthanide chemistry.[20] **3** can be considered as product of two nonanuclear clusters such as $[Y_9O_2(OH)_8(aacac)_{16}]^-$[23] (aacac = allylacetoacetate) and $[Ln_9O_2(OH)_8(BA)_{16}]^-$[20] (BA = benzoylacetone, Ln = Sm, Eu, Gd, Dy, Er), sharing their base square-pyramidal units (Scheme 1). The nonanuclear clusters themselves can be regarded as being composed of two $[Ln_5(\mu_4-O)(\mu_3-OH)_4]^{9+}$ units, which are sharing the apical lanthanide ion of the pentanuclear square-pyramidal units. Pentanuclear clusters such as $[Eu_5(OH)_5-(DBM)_{10}]$ (DBM = dibenzoylmethanid) have been reported earlier.[21]

(17) The collected dataset for **3a** is poor. Therefore, only the cell constants are given. $C_{144}H_{114}Dy_{14}N_{24}O_{90}$, tetragonal, *P4/nnc* (no. 126); lattice constants $a = 19.770(9)$, $c = 34.009(9)$ Å; $V = 13293(9)$ Å³, $Z = 2$.
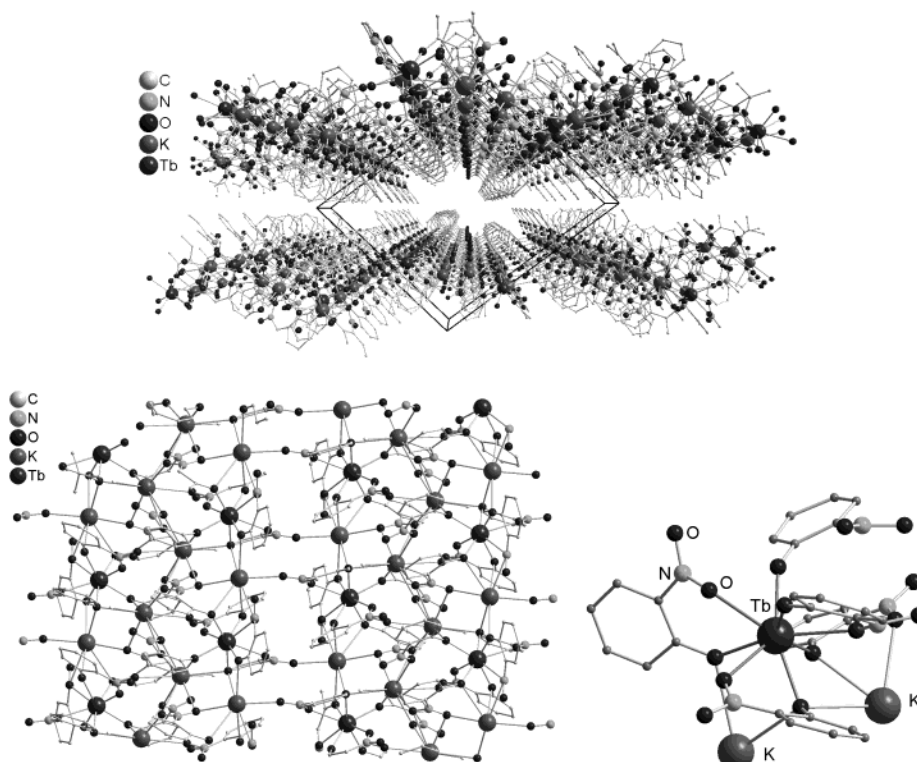(18) Evans, W. J.; Sollberger, M. S. *Inorg. Chem.* **1988**, *27*, 4417−4423.
(19) Wang, R.; Zheng, Z.; Jin, T.; Staples, R. J. *Angew. Chem.* **1999**, *111*, 1929−1931; *Angew. Chem., Int. Ed.* **1999**, *38*, 1813−1815.

(20) Xu, G.; Wang, Z.-M.; He, Z.; Lu, Z.; Liao, C.-S.; Yan, C.-H. *Inorg. Chem.* **2002**, *41*, 6802−6807.
(21) Xiong, R.-G.; Zuo, J.-L.; Yu, Z.; You, X.-Z.; Chen, W. *Inorg. Chem. Commun.* **1999**, *2*, 490−494.

Figure 4. Top: Solid-state structure of **4**. Bottom left: View to a single sheet from above. Bottom right: Shown is one unit out of the polymeric structure and the atom labeling scheme, omitting hydrogen atoms.

It is well-known that the most stable lanthanide clusters are oxo/hydroxo clusters. Basically two different approaches toward the preparation of oxo/hydroxo clusters were investigated. One way to obtain these compounds is the hydrolysis of moisture sensitive starting material as it is described in this contribution, whereas the other approach is a hydrolytic one in which the water molecules are deprotonated in a controlled manner.[13,19] Most of the oxo/hydroxo clusters are stabilized by ligands such as alkoxides,[22] β-diketones,[23,24] and amino acids.[13] The use of nitrophenoles as ligand best to our knowledge is unique in lanthanide chemistry. Although no structural investigations on lanthanide *o*-nitrophenoles are known but there are a number of publications dealing with lanthanide picrates.[25] Most of these compounds, which were prepared in water, are mono- or dinuclear complexes.

Infinite Layers. Reaction of **1** with anhydrous terbium trichlorides in a 5:1 molar ratio in THF followed by crystallization from THF/*n*-pentane (1:4) afforded infinite layers of composition $[[K_2(o\text{-}O_2N\text{-}C_6H_4\text{-}O)_5Tb]_n]$ (**4**) as red crystals (eq 3). Using other stoichiometric ratios led to the same product. The solid-state structure of **4** was established by single-crystal X-ray diffraction (Figure 4). As a result of the larger ion radius of terbium, there are in contrast to **2** not four but five *o*-nitrophenolate ligands coordinated to the
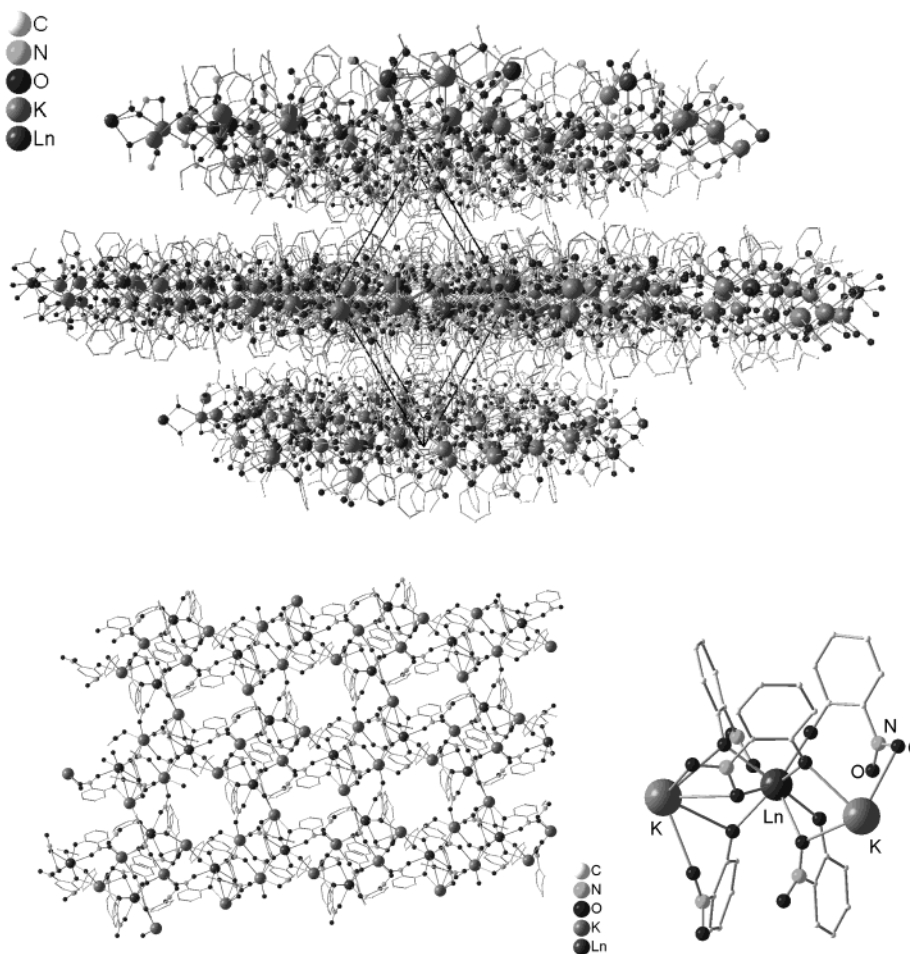
Scheme 1. Schematic Chart of the Pentanuclear $[Ln_5(\mu_4\text{-}O)(\mu_3\text{-}OH)_4]^{9+}$ Unit (a), Which Can Be Considered as a Building Block for Nonanuclear (b) and Tetradecanuclear Clusters (c)
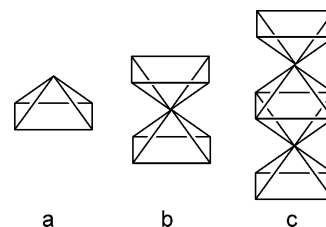
metal atom. Nevertheless, the coordination number of terbium is still eight. Thus, three *o*-nitrophenolate anions act as bidentate ligands, whereas two of them just coordinate via the phenoxy group. The coordination polyhedron can be considered as a distorted square-antiprism. The Tb−O bond lengths are in the range of 2.256(8)−2.334(8) Å for Tb−OR and 2.531(7)−2.574(6) Å for Tb−ONO. To balance the charge to each $[(o\text{-}O_2N\text{-}C_6H_4\text{-}O)_5Tb]^{2-}$ unit, two potassium counterions are coordinated via the nitro groups.[16] The coordination environment of both potassium atoms is different. Thus K1 is 7-fold coordinated, whereas K2 is surrounded by eight oxygen atoms. In comparison to **2**, as a result of the increased number of potassium atoms per lanthanide atom in **4**, more connections between the $[(o\text{-}O_2N\text{-}C_6H_4\text{-}O)_xLn]^{n-}$ units are observed. This increased connectivity causes the change in the microstructure from infinite chains in **2** to an infinite layer in **4**.
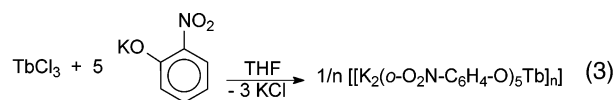
(22) (a) Bradley, D. C.; Mehrotra, R. C.; Gauer, D. P. *Chem. Rev.* **1991**, *91*, 1287. (b) Hubert-Pfalzgraf, L. G. *Coord. Chem. Rev.* **1998**, *178−180*, 967−997.
(23) Hubert-Pfalzgraf, L. G.; Miele-Pajot, N.; Papernik, R.; Vaissermann, J. *J. Chem. Soc., Dalton Trans.* **1999**, 4127−4130.
(24) (a) Mehrotra, R. C.; Bohra, R.; Gaur, D. P. *Metal β-Diketonates and Allied Derivatives*; Academic Press: London, 1978. (b) Guillon, H.; Hubert-Pfalzgraf, L. G.; Vaissermann, J. *Eur. J. Inorg. Chem.* **2000**, 1243−1252.
(25) (a) Ayala, J. D.; Zinner, L. B.; Vicentini, G.; Del Pra, A.; Bomberieri, G. *Inorg. Chim. Acta* **1993**, *211*, 161−166. (b) Harrowfield, J. M.; Weimin, L.; Skelton, B. W.; White, A. H. *Aust. J. Chem.* **1994**, *47*, 321−337.

$$TbCl_3 + 5 \quad \underset{\text{THF}}{\overset{}{\xrightarrow{}}} \quad 1/n\,[[K_2(o\text{-}O_2N\text{-}C_6H_4\text{-}O)_5Tb]_n] \quad (3)$$
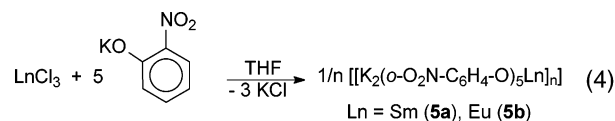
Figure 5. Top: Solid-state structure of **5**. Bottom left: View to a single sheet from above. Bottom right: Shown is one unit out of the polymeric structure and the atom labeling scheme, omitting hydrogen atoms (Ln = Sm, Eu).

Since we learned about the dramatic change in the microstructure by just altering the ion radius of the lanthanide, we were interested to use even larger center metals. Reaction of **1** with anhydrous europium and samarium trichloride in THF under conditions described above and subsequent crystallization from THF/*n*-pentane (1:4) led to infinite layers of composition $[[K_2(o\text{-}O_2N\text{-}C_6H_4\text{-}O)_5Ln)]_n]$ (Ln = Sm (**5a**), Eu (**5b**)) (eq 4). Compounds **5a** and **5b** are isostructural. As seen from the solid-state structures of **5a** and **5b**, which were established by single-crystal X-ray diffraction (Figure 5) also infinite layers are formed. As observed in **4**, five *o*-nitrophenolates ligands are coordinated to the metal atom. Even samarium and europium have the larger ion radii than terbium, surprisingly the center metals are only 7-fold coordinated. Thus, two *o*-nitrophenolate anions act as bidentate ligands, whereas the remaining ligands coordinate via the phenoxy groups only. The Ln−O bond distances range for Ln−OR from 2.297(4) to 2.368(4) Å (**5a**) and from 2.296(6) to 2.360(6) Å (**5b**) and for Ln−ONO from 2.500(5) to 2.574(4) Å (**5a**) and from 2.488(6) to 2.584(6) Å (**5b**). These distances are in a similar range compared to those observed in the terbium compound **4** (Tb−OR, 2.256(8)−2.334-(8) Å; and Tb−ONO, 2.531(7)−2.574(6) Å).

In comparison to **4**, not only is the lanthanide atom lower coordinated but also the potassium atoms are exclusively coordinated by the nitro groups. Thus K1 is 7-fold coordinated and K2 features just a coordination number of six.[16] The lower coordination numbers of both sorts of metals in **5a** and **5b** cause

in comparison to **4** a more open structure. In compounds **5a** and **5b**, channels rectangular through the layers are observed. Inside the channels there are solvent molecules. These are disordered in the single X-ray structures and were assigned as *n*-pentane. Investigations on the luminescence properties on **5b** did not show any useful result.

$$LnCl_3 + 5 \quad KO\!\!-\!\!\langle\!\!\langle\ \rangle\!\!\rangle\!\!-\!\!NO_2 \xrightarrow[-\ 3\ KCl]{THF} 1/n\ [[K_2(o\text{-}O_2N\text{-}C_6H_4\text{-}O)_5Ln]_n] \quad (4)$$
$$Ln = Sm\ (\textbf{5a}),\ Eu\ (\textbf{5b})$$

Summary

In summary, it can be emphasized that *o*-nitrophenolate is a versatile ligand, which can coordinate in a chelating and in a metal bridging mode to different metals. Thus, the reactions of potassium *o*-nitrophenolate with anhydrous yttrium and lanthanide trichlorides give coordination polymers and oligomers, respectively. By using the smaller lanthanides as center metals infinite chains are obtained, when the reactions are performed under rigorous exclusion of air. The chains consist of $[(o\text{-}O_2N\text{-}C_6H_4\text{-}O)_4Ln]^-$ metalate anions, which are bridged by the potassium counterions. Using the same reaction conditions but performing the crystallization in air leads to partial hydrolysis. The obtained products are tetradecanuclear lanthanide clusters. By increasing the ion radius of the metal, the microstructure of the coordination polymers changes. When samarium, europium,

and terbium are used as center metals, infinite layers are obtained. The layers consist of $[(o\text{-}O_2N\text{-}C_6H_4\text{-}O)_5Ln]^-$ metalate anions, which are bridged by two potassium counterions. The structure of the layers depends on the nature of the center metal used. Thus, layers having terbium as a center metal have a closer packing than those with samarium and europium. The closer packing is a result of the increased coordination number of the lanthanide metal and the potassium atoms. In contrast, the lower coordination numbers in the samarium and europium compound give a more open structure in which channels rectangular through the layers are observed. Inside the channels, solvent molecules are localized.

Supporting Information Available: Experimental details (PDF) and X-ray crystallographic files in CIF format for the structure determinations of **1**, **2b**, **2c**, **3a**, **3c**, **4**, **5a**, and **5b**. This material is available free of charge via the Internet at http://pubs.acs.org.

JA0396044