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Lanthanide–Potassium Wheels

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Mixed potassium–lanthanide wheel-shaped-structured, hexanuclear coordination oligomers of composition $[(\eta^5\text{-}C_5H_5)Ln(NPh_2)_2\{N(PPh_2)_2\}_2K_2(THF)_4]_2$ (Ln = Er (**1a**), Yb (**1b**)) and an octanuclear coordination polymer of composition $[(\eta^5\text{-}C_5H_5)Sm(NPh_2)_2\{N(PPh_2)_2\}K]_\infty$ (**2**) were synthesized. All presented compounds can be obtained in moderate yields in a *one-pot* procedure, in which the potassium salts $KNPh_2$ and $[K(THF)_nN(PPh_2)_2]$ as well as NaC_5H_5 are reacted with anhydrous samarium, erbium, and ytterbium trichloride in THF.

The construction of coordination polymers and oligomers has been a field of rapid growth in supramolecular and material chemistry because of the formation of fascinating structures and their 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] In contrast, in lanthanide chemistry the large ions generally display variable and high coordination 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 the use of their d-block metal analogues.[3] Recently, a few coordination polymers have appeared on lanthanide-based frameworks employing polydentate ligands such as sulfoxides,[4] carboxylates,[5] pyridones,[6] lactames,[7] and 4,4′-bipyridine-*N*,*N*′-dioxide.[8] In contrast, coordination oligomers based on wheel-shaped structures usually are formed in the presence of either bulky ligands,[9,10] interstitial atoms,[11] or both. In these structures, the wheel is normally built up by one kind of metal atom.

Recently, we reported an approach in which lanthanide coordination oligomers and polymers (chains and layers) can be built up by using relatively small ligands.[12] As a result of the insufficient shielding of the lanthanide atom, metalate complexes are formed. By using suitable polydentate ligands, these metalate complexes can be connected via the counterion, thus forming coordination polymers. The shape of the polymer depends on the ligand and on the ion radius of the lanthanide atom. Other groups have shown previously that anionic lanthanide phenoxides[13,14] and pyrazolates[15] may form chains and layers by π coordination of the aromatic

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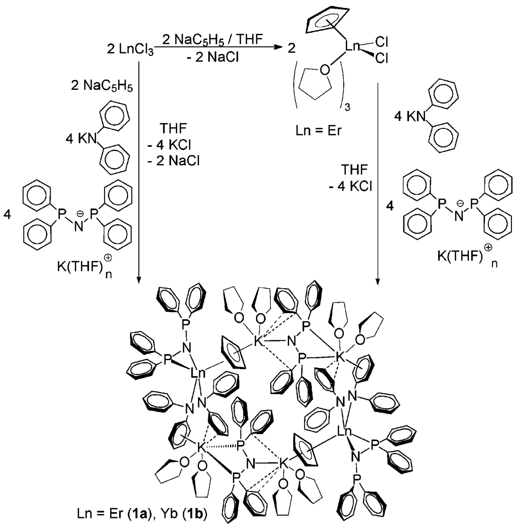
Scheme 1



ring onto the counterion. Herein we report an approach in which wheel-shaped structures of potassium and lanthanide atoms are obtained by using small ligands, which bridge the metal atoms by π coordination to aromatic rings.

Reaction of [(η^5-C_5H_5)$ErCl_2$] with the amido compounds $KNPh_2$ and [K(THF)$_n$N(PPh_2)$_2$] (n = 1.25 and 1.5)[16] in THF and crystallization from THF/n-pentane (1:2) lead to the hexanuclear, wheel-shaped-structured compound [(η^5-C_5H_5)Er(NPh_2)$_2${N(PPh_2)$_2$}$_2$$K_2(THF)_4$]$_2$ (**1a**). Compound **1a** and the Yb analogue, **1b**, can also be obtained in moderate yield in a *one-pot* reaction, in which the potassium salts $KNPh_2$ and [K(THF)$_n$N(PPh_2)$_2$], as well as NaC_5H_5, are reacted with anhydrous erbium or ytterbium trichloride in THF, followed by crystallization from THF/pentane (Scheme 1).[17,18] The solid-state structures of the new complexes were established by single-crystal X-ray diffraction.[19] The lanthanide ion of **1a**,**b** is surrounded by four ligands, resulting in a metalate substructure of composition [(η^5-C_5H_5)Ln(NPh_2)$_2${N(PPh_2)$_2$}]$^-$. The whole ring of **1a**,**b** consists basically of two [K(THF)$_2$-(η^5-C_5H_5)Ln(NPh_2)$_2${N(PPh_2)$_2$}] and two [K(THF)$_2$N(PPh_2)$_2$] units. In contrast to most other metalate complexes, the cations not only are surrounded by solvent molecules but also coordinate via a π interaction onto the [(η^5-C_5H_5)Ln-(NPh_2)$_2${N(PPh_2)$_2$}]$^-$ unit. K1 is η^5-coordinated onto the C_5H_5 ring, whereas K2 is η^2- and η^6-coordinated onto the phenyl ring of the NPh_2 group. As a result of the electrostatic interactions between the aromatic rings and the potassium ions, the K−C distances vary over a wide range. In Figure 1, all C−K interactions up to a value of 350 pm, a conservative limit for K−C interactions, are marked as dotted lines.[13] A comparable bridging via an NPh_2 group was observed in the monomeric complexes [(THF)$_2$Na(Ph_2N)$_2$-Ln{N($SiMe_3$)$_2$}$_2$] (Ln = Gd, Yb).[20]

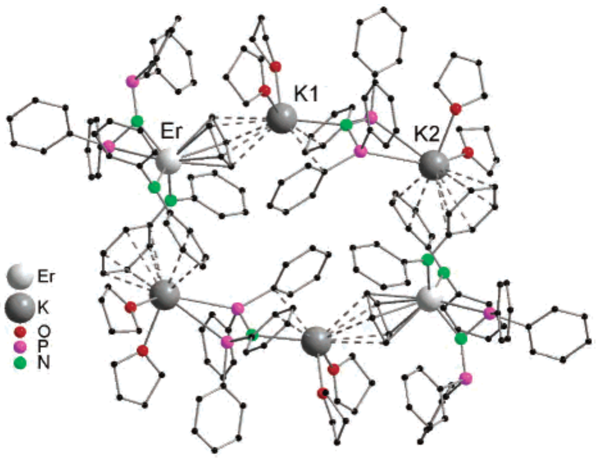


Figure 1. Solid-state structure of **1a** showing the atom labeling scheme, omitting hydrogen atoms.

In the {K(THF)$_2$−N(PPh_2)$_2$−K(THF)$_2$}$^+$ unit, K1 binds to the nitrogen atom whereas K2 interacts with the phosphorus atoms. A similar structural motive is found in the starting material [K(THF)$_{1.5}$N(PPh_2)$_2$].[16] Also some π interactions to the phenyl rings are observed. Thus, the {K-(THF)$_2$−N(PPh_2)$_2$−K(THF)$_2$}$^+$ unit can be considered as a cutout of the solid-state structure of [K(THF)$_{1.5}$N(PPh_2)$_2$]. The magnetic properties of compound **1a**,**b** show a weak antiferromagnetic interaction.[21]

By using the same reaction conditions as those for the synthesis of **1a**,**b** but performing the synthesis with samarium as the center metal and later optimizing the stoichiometric ratios, one obtains a coordination polymer of composition [(η^5-C_5H_5)Sm(NPh_2)$_2${N(PPh_2)$_2$}K]$_\infty$ (**2**) in moderate yields

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(17) The bonding situation in the schemes is simplified for clarity.

(18) Synthesis of [(η^5-C_5H_5)Ln(NPh_2)$_2${N(PPh_2)$_2$}$_2$$K_2(THF)_4$]$_2$ (Ln = Er (**1a**), Yb (**1b**)). Route A: A total of 20 mL of THF was added to a mixture of 150 mg (0.55 mmol) of $ErCl_3$ and 44 mg (0.50 mmol) of NaC_5H_5, and the mixture was stirred for 18 h at room temperature. The mixture was filtered and the solvent taken off in vacuo. A total of 207 mg (1.00 mmol) of $KNPh_2$ and 20 mL of THF were added to the remaining residue, and the mixture was stirred for another 6 h at room temperature. Then, again the solvent was taken off in vacuo and 500 mg (1.00 mmol) of [K(THF)$_n$N(PPh_2)$_2$] was added. Then 20 mL of THF was added to the remaining residue. After stirring for another 18 h, the mixture was filtered and the filtrate concentrated. After the addition of n-pentane, pink crystalline plates were obtained. Route B: A total of 20 mL of THF was added to a mixture of 0.73 mmol of $LnCl_3$, 64 mg (0.73 mmol) of NaC_5H_5, 730 mg (1.46 mmol) of [K(THF)$_n$N(PPh_2)$_2$], and 303 mg (1.46 mmol) of $KNPh_2$, and the mixture was stirred for 16 h at room temperature. Then the mixture was filtered and the filtrate concentrated. After the addition of n-pentane, crystalline plates were obtained. **1a**. Yield: 56% (route B), pink crystals. IR (KBr [cm^{-1}]): 3051 (w, $\nu_{C=CH}$), 2994 (w, ν_{CH}), 2914 (m, ν_{CH}), 1576 (s, $\nu_{C=C}$), 1480 (s), 1431 (s), 1293 (m), 1093 (w), 986 (m, ν_{PC}), 972 (m), 896 (m), 749 (s), 739 (s), 697 (vs). Anal. Calcd for $C_{186}H_{194}Er_2K_4N_8O_8P_8 \cdot 2C_4H_8O$ (3480.45): C, 65.59; H, 5.96; N, 3.15. Found: C, 65.49; H, 5.87; N, 3.27. **1b**. Yield: 36% (route B), red crystals. IR (KBr [cm^{-1}]): 3045 (w, $\nu_{C=CH}$), 2994 (w, ν_{CH}), 2975 (m, ν_{CH}), 2870 (m), 1577 (s, $\nu_{C=C}$), 1482 (s), 1431 (s), 1290 (s), 986 (sh, ν_{PC}), 972 (s), 896 (m), 748 (s), 736 (s), 697 (vs). Anal. Calcd for $C_{186}H_{194}K_4N_8O_8P_8Yb_2 \cdot 2C_4H_8O$ (1781.97): C, 65.38; H, 5.94; N, 3.14. Found: C, 65.17; H, 5.86; N, 3.14.

(19) Single-crystal X-ray diffraction data: **1a** ($C_{97}H_{105}ErK_2N_4O_5P_4$ (1776.19) = 0.5 **1a**·THF), Brucker Smart 1000 CCD, space group $P1$ (No. 2) with a = 13.450(3) Å, b = 17.818(3) Å, c = 20.331(4) Å, α = 66.649-(5)°, β = 83.754(5)°, γ = 77.588(5)° at 173 K, Z = 2, V = 4367.3-(15) Å^3, ρ = 1.351 g cm^{-3}, $2\theta_{max}$ = 61°, 54523 reflections collected, 26299 independent reflections (R_{int} = 0.0562). The structure was solved by Patterson methods (SHELXS-97[24] and SHELXL-97[25]) and refined by full-matrix least-squares techniques using 13667 reflections with $I > 2\sigma(I)$ to R1 = 0.0582 and wR2 = 0.1495.

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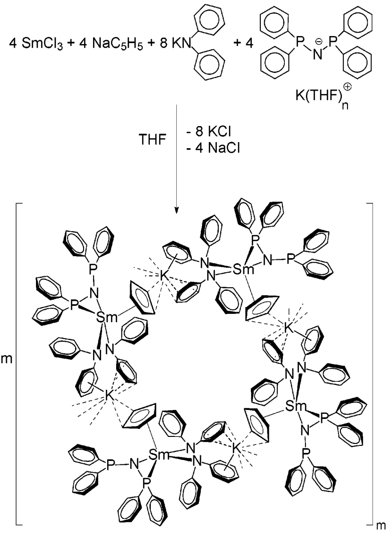
Scheme 2



(Scheme 2).[17,22] For compound **2,** the solid-state structure was established by single-crystal X-ray diffraction (Figure 2).[23] Compound **2** can be considered as an octanuclear, wheel-shaped-structured Sm$_4$K$_4$ compound, in which the potassium cations bridge the $[(\eta^5\text{-C}_5\text{H}_5)\text{Sm(NPh}_2)_2\{\text{N(PPh}_2)_2\}]^-$ metalate anions (Figure 2). In the center of the ring rectangular to the ring plane, a crystallographic C_4 axis is observed. In Figure 2, all C−K interactions up to an arbitrary range of 3.5 Å are marked as dotted lines.[13] By using these criteria, potassium is η^2-coordinated by the C$_5$H$_5$ ring and η^4- and η^6-coordinated to the phenyl rings of the NPh$_2$ groups. Moreover, potassium also is η^6-coordinated onto one phenyl ring of an NPh$_2$ group of a neighboring $[(\eta^5\text{-C}_5\text{H}_5)\text{Sm(NPh}_2)_2\{\text{N(PPh}_2)_2\}]^-$ unit, thus acting as a knot between the octanuclear wheel-shaped-structured Sm$_4$K$_4$ units (Figure 2). In contrast to compound **1a**,**b**, which consists of isolated rings, in compound **2** the rings are connected to each other, thus forming a three-dimensional polymeric structure. The average C−K distance is 331.5(9) pm, which clearly shows the weak electrostatic interaction in the molecule. Compared to compound **1a**,**b**, no THF molecules are coordinated to the potassium ions. This is a result of the increased number of π interactions to the aromatic rings. In contrast to **1a**,**b**, the bridging between the potassium atoms and the metalate units takes place exclusively via the (NPh$_2$)$^-$ group and the $(\eta^5\text{-C}_5\text{H}_5)^-$ ring. The $\{\text{N(PPh}_2)_2\}^-$ ligand is not involved.

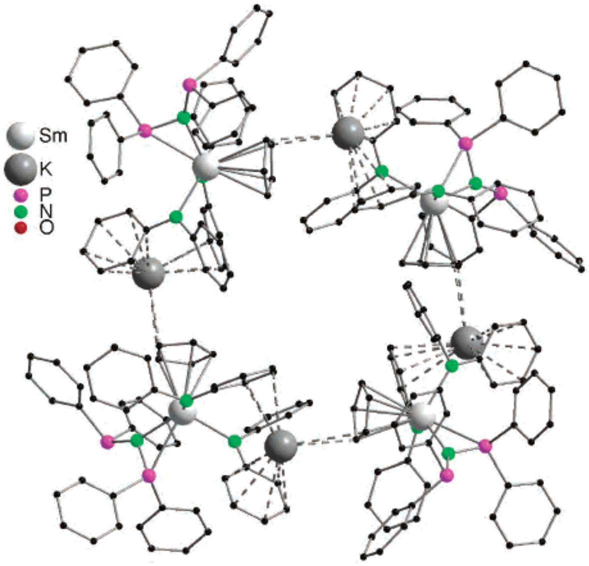


Figure 2. Solid-state structure of **2** showing the atom labeling scheme, omitting hydrogen atoms.

In summary, it can be emphasized that the reaction of anhydrous samarium, erbium, and ytterbium trichloride with relatively small potassium amido compounds, which contain some phenyl rings, gives unusual products. Metalate complexes are formed as a result of the insufficient shielding of the lanthanide atom by the small ligands. By using suitable ligands, these metalate complexes are connected to each other via the potassium ion. The cation bridges the metalate units via π coordination to aromatic rings, thus forming wheel-shaped-structured coordination oligomers and polymers. The shape of the microstructure seems to depend on the ionic radius of the lanthanide atom. To the best to our knowledge of coordination chemistry, the setup of the presented potassium lanthanide wheel-shaped-structured coordination oligomer and polymer is unique.

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

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(22) Synthesis of $[(\eta^5\text{-C}_5\text{H}_5)\text{Sm(NPh}_2)_2\{\text{N(PPh}_2)_2\}\text{K}]_\infty$ (**2**): A total of 20 mL of THF was added to a mixture of 100 mg (0.39 mmol) of SmCl$_3$, 34 mg (0.39 mmol) of NaC$_5$H$_5$, 194 mg (0.39 mmol) of [K(THF)$_n$N(PPh$_2$)$_2$], and 162 mg (0.78 mmol) of KNPh$_2$, and the mixture was stirred for 16 h at room temperature. Then the mixture was filtered and the filtrate concentrated. After the addition of *n*-pentane, yellow crystalline prisms were obtained. Yield: 98 mg (24%), yellow crystals. IR (KBr [cm^{-1}]): 3050 (w, $\nu_{\text{C=CH}}$), 2998 (m, ν_{CH}), 2979 (m, ν_{CH}), 1576 (s, $\nu_{\text{C=C}}$), 1481 (s), 1431 (s), 1293 (s), 1093 (m), 986 (m, ν_{PC}), 972 (m), 896 (m), 749 (s), 738 (s), 695 (m). Anal. Calcd for C$_{56}$H$_{56}$ClN$_2$O$_2$P$_4$Yb (1121.40): C, 59.98; H, 5.03; N, 2.50. Found: C, 59.91; H, 4.89; N, 2.31. Anal. Calcd for C$_{53}$H$_{45}$KN$_3$P$_2$Sm·C$_4$H$_8$O (1047.41): C, 65.36; H, 5.10; N, 4.01. Found: C, 65.04; H, 5.13; N, 3.96.

(23) Single-crystal X-ray diffraction data: **2** (C$_{57}$H$_{53}$KN$_3$OP$_2$Sm (1047.41) = **2**·THF), Brucker Smart 1000 CCD, space group $I4_1/a$ (No. 88) with $a = 29.512(5)$ Å, $c = 23.318(7)$ Å at 173 K, $Z = 16$, $V = 20310(8)$ Å^3, $\rho = 1.370$ g cm^{-3}, $2\theta_{\text{max}} = 46.5°$, 68159 reflections collected, 7305 independent reflections ($R_{\text{int}} = 0.1287$). The structure was solved by Patterson methods (SHELXS-97[24] and SHELXL-97[25]) and refined by full-matrix least-squares techniques using 5163 reflections with $I > 2\sigma(I)$ to R1 = 0.0509 and wR2 = 0.1745. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as a supplementary publication no. CCDC-248516 (**1**) and -248517 (**2**). Copies of the data can be obtained free of charge upon application to CCDC, 12 Union Road, Cambridge CB21EZ, U.K. (fax +(44)-1223-336-033; e-mail deposit@ccdc.cam.ac.uk).

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