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Novel Anionic Lanthanocene Amide Complexes: Syntheses and X-ray Crystal Structures of $[Na(THF)_2(\mu\text{-}\eta^5{:}\eta^5\text{-}MeC_5H_4)_2Ln(NPh_2)_2]_n$ (Ln = Sm, Er)

Yaorong Wang and Qi Shen*

School of Chemistry and Chemical Engineering, Suzhou University,
Suzhou 215006, People's Republic of China

Feng Xue

Department of Chemistry, The Chinese University of Hong Kong, Hong Kong

Kaibei Yu

Chengdu Institute of Organic Chemistry, Academia Sinica,
Chengdu 610041, People's Republic of China

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Treatment of $(MeC_5H_4)_2LnCl$ with $NaNPh_2$ in THF affords the supramolecular amide complexes $[Na(THF)_2(\mu\text{-}\eta^5{:}\eta^5\text{-}MeC_5H_4)_2Ln(NPh_2)_2]_n$ (Ln = Sm (**1**), Er (**2**)). Both complexes have an alternating −Cp−Ln−Cp−Na− chain structure, and each lanthanide atom is coordinated with two η^5-MeC_5H_4 rings and two NPh_2, while Na is coordinated by two η^5-MeC_5H_4 rings and two THF without interacting with any amido ligands.

Introduction

The lanthanocene amides have recently attracted considerable attention as catalysts or precatalysts in a variety of homogeneous processes.[1−5] However, the synthesis and molecular structure of lanthanocene amides is still underdeveloped. Only a few neutral and ionic organolanthanide amide complexes have been reported in the literature such as $(C_5Me_5)_2LnNHR(H_2NR)$ (Ln = La, Nd),[1] $[Me_2Si(C_5Me_4)(C_5H_3\text{-neomenthyl})]LnN(SiMe_3)_2$ (Ln = Y, La, Sm, Lu),[6] $(MeC_5H_4)_2LnN(i\text{-}Pr)_2(THF)$ (Ln = Y, Er, Yb),[5] $(MeC_5H_4)_2LnNC_5H_{10}(HC_5H_{10})$ (Ln = Y, Er, Yb),[3b] $(C_5Me_5)_2YN(SiMe_3)_2$,[7] $[(MeC_5H_4)_2Yb(\mu\text{-}NH_2)]_2$,[8] and $[Li(DME)_3][(C_5H_5)_2Nd(NPh_2)_2]$.[9] Here we report the "self-assembly" of supramolecular lanthanide amide complexes bearing both diphenylamido and methylcyclopentadienide ligands in which sodium becomes incorporated into the complex via bridging interactions of two η^5-$CH_3C_5H_4$ with lanthanide atoms.

Results and Discussion

Recent studies on the synthesis of lanthanocene diphenylamides have shown that ion pair complexes $[LiL_{3-4}][Cp_nLn(NPh_2)_{4-n}]$ (n = 1, 2; L = THF, DME) are commonly isolated from the reaction of lanthanocene chloride with $LiNPh_2$[9−11] or the reaction of methyl-bridged organolanthanide alkyls $(C_5H_5)_2Ln(\mu\text{-}Me)_2Li(tmed)$ with diphenylamine.[12] We are interested in understanding whether the structure of diphenylamide complexes will be changed if sodium diphenylamide is used as reagent.

Reaction of $(MeC_5H_4)_2SmCl$ with 1 equiv of $NaNPh_2$, which was formed by the reaction of NaH and $HNPh_2$ in THF,[13] affords a novel amide complex $[Na(THF)_2(MeC_5H_4)_2Sm(NPh_2)_2]_n$ in 32.5% yield. The yield can be improved to 63% when the molar ratio of $NaNPh_2$ to $(MeC_5H_4)_2SmCl$ increases to 2. The same reaction with $(MeC_5H_4)_2ErCl$ gives results similar to those shown in the following equation.

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* To whom correspondence should be addressed. E-mail: qshen@suda.edu.cn.

(1) Gagne, M. R.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 275.

(2) Giardello, M. A.; Yamamoto, Y.; Brard, L.; Marks, T. J. *J. Am. Chem. Soc.* **1995**, *117*, 3276.

(3) (a) Mao, L.; Shen, Q. *J. Polym. Sci. Part A: Polym. Chem.* **1998**, *36*, 1593. (b) Mao, L.; Shen, Q.; Sun, J. *J. Organomet. Chem.* **1998**, *566*, 9.

(4) Hultzsch, K. C.; Spaniol, T. P.; Okuda, J. *Organometallics* **1997**, *16*, 4845.

(5) Mao, L.; Shen, Q.; Xue, M.; Sun, J. *Organometallics* **1997**, *16*, 3711.

(6) Giardello, M. A.; Conticello, V. P.; Brard, L.; Sabat, M.; Rheingold, A. L.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10212.

(7) den Haan, K. H.; de Boer, J. L.; Teuben, J. H.; Spek, A. L.; Kojic-Prodic, B.; Hays, G. R.; Huis, R. *Organometallics* **1986**, *5*, 1726.

(8) Hammel, A.; Weidlein, J. *J. Organomet. Chem.* **1990**, *388*, 75.

(9) Guan, J.; Shen, Q.; Jin, S.; Lin, Y. *Polyhedron* **1994**, *13*, 1695.

(10) (a) Mao, L.; Shen, Q.; Jin, S. *Polyhedron* **1994**, *13*, 1023. (b) Mao, L.; Shen, Q.; Lin, Y. *Youji Huaxue* **1994**, *14*, 215.

(11) Guan, J.; Jin, S.; Lin, Y.; Shen, Q. *Organometallics* **1992**, *11*, 2483.

(12) Schumann, H.; Palamidis, E.; Loebel, J. *J. Organomet. Chem.* **1990**, *390*, 45.

(13) Minhas, R. K.; Ma, Y.; Song, J. I.; Gamborotta, S. *Inorg. Chem.* **1996**, *35*, 1866.

10.1021/om9906215 CCC: $19.00

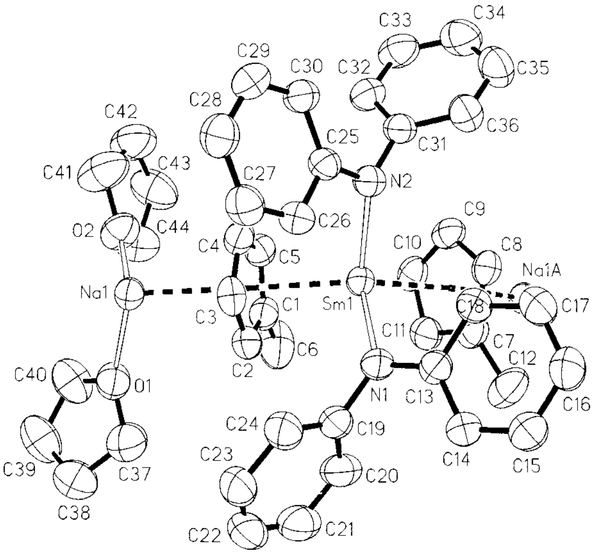

Figure 1. Molecular structure of $[Na(THF)_2(\mu\text{-}\eta^5{:}\eta^5\text{-}MeC_5H_4)_2Sm(NPh_2)_2]_n$ with atomic numbering (hydrogen atoms have been omitted for clarity).

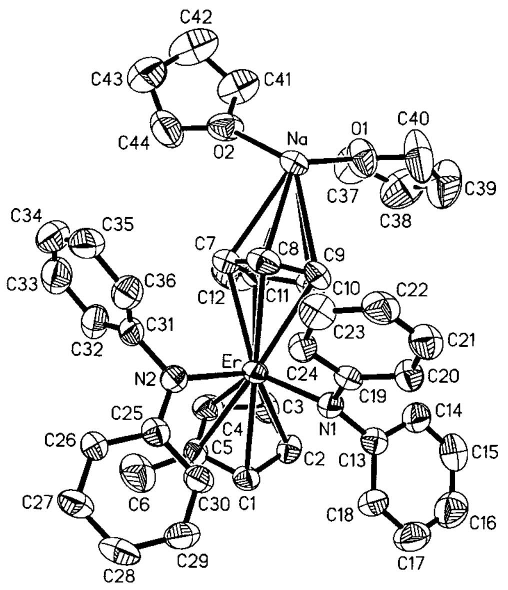

Figure 2. Molecular structure of $[Na(THF)_2(\mu\text{-}\eta^5{:}\eta^5\text{-}MeC_5H_4)_2Er(NPh_2)_2]_n$ with atomic numbering (hydrogen atoms have been omitted for clarity).

$$(MeC_5H_4)_2LnCl + 2NaNPh_2 \rightarrow (1/n)[Na(THF)_2(MeC_5H_4)_2Ln(NPh_2)_2]_n + NaCl \quad (Ln = Sm\ (\mathbf{1}),\ Er\ (\mathbf{2}))$$

The two complexes were identified by single-crystal X-ray diffraction studies to be isostructural and have an unusual structure.

Figure 1 and Figure 2 show the most striking structural feature of complexes **1** and **2**. The two complexes possess a supramolecular structure composed of units of $[Na(THF)_2(\mu\text{-}\eta^5{:}\eta^5\text{-}MeC_5H_4)_2Ln(NPh_2)_2]$ which are connected together via bridging η^5-MeC_5H_4 groups, generating an alternate −Cp−Ln−Cp−Na− backbone. The zigzag chains extend along the *a* axis and are parallel (Figure 3). To our best knowledge, organolanthanide complexes with η^5-cyclopentadienyl groups as bridged ligands to connect Ln and alkali metals together in a supramolecule are extremely rare. Only four examples, $[NaYb(C_5H_5)_3]$,[14] $Na\{[1,3\text{-}(Me_3Si)_2C_5H_3]Yb^{II}\}_2(\mu\text{-}I)$,[15] $\{K[(\mu\text{-}C_5H_5)_2Nd(\mu\text{-}OAr)_2]\}_n$,[16] and $[(\mu,\eta^5\text{-}C_5Me_5)Sm(OAr)(\mu,\eta^5\text{-}C_5Me_5)K(THF)_2]_n$,[17] were reported so far. The former two complexes are homoleptic cyclopentadienyl complexes. The later two are heteroleptic ones with an aryloxide ligand. So this is the first example of supramolecular lanthanocene amides with η^5-Cp as bridging ligand.

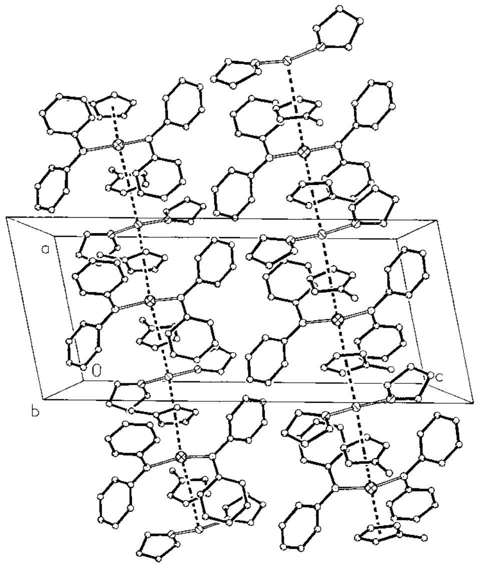

Figure 3. Unit cell of $[Na(THF)_2(\mu\text{-}\eta^5{:}\eta^5\text{-}MeC_5H_4)_2Ln(NPh_2)_2]_n$ (Ln = Sm, Er).

The coordination around sodium is special. There are only two η^5-MeC_5H_4 and two THF but no NPh_2 surrounding the sodium atom, although this is a sodium diphenylamide complex. A similar structural feature has been found in $\{K[(\mu\text{-}C_5H_5)_2Nd(\mu\text{-}OAr)_2]\}_n$.[16]

The coordination geometries around the metals in complex **1** and **2** are the conventional distorted tetrahedrons. A line between the center of the Cp rings and the metal atoms is severely bent (C(ring centroid)−Na−C(ring centroid) 125.1° for **1**, 125.9° for **2** and C(ring centroid)−Ln−C(ring centroid) 122.7° for **1**, 123.8° for **2**. The selected bond distances and angles for **1** and **2** are listed in Tables 1 and 2. The Ln−C(ring) average distance of 2.771 Å in **1** is similar to 2.696 Å in **2** and 2.79(6) Å in $\{K[(\mu,\eta^5\text{-}C_5H_5)_2Nd(\mu\text{-}OAr)_2]\}_n$[16] when the differences in radial size for Sm^{3+}, Er^{3+}, and Nd^{3+} were considered.[18] The Ln−N distances (2.374(3), 2.377(3) Å) for **1** are similar to 2.286(6), 2.288(6) Å for **2**. They are comparable to the 2.290(7), 2.293(7) Å in $[Li(THF)_4][(C_5H_5)_2Lu(NPh_2)_2]$[12] and the 2.421(7), 2.434(7) Å in $[Li(DME)_3][(C_5H_5)_2Nd(NPh_2)_2]$,[9] if corrections are made for trivalent eight-coordinate ionic radii.[18]

The Na−C(ring) distances are in the range 2.745−2.978 Å for **1** and 2.741−2.969 Å for **2**. As expected, the average Na−C(ring) distances (2.872 Å for **1**, 2.865 Å

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(14) Apostolidis, C.; Deacon, G. B.; Dornberger, E.; Edelmann, F. T.; Kanellakopulos, B.; Mackinnon, P.; Stalke, D. *Chem. Commun.* **1997**, 1047.

(15) Voskoboynikov, A. Z.; Agarkov, A. Y.; Shestakova. A. K.; Beletskaya, I. P.; Kuz'mina, L. O.; Howard, J. A. K. *J. Organomet. Chem.* **1997**, *544*, 65.

(16) Evans, W. J.; Ansar, M. A.; Khan, S. I. *Organometallics* **1995**, *14*, 558.

(17) Hou, Z.; Zhang, Y.; Yoshimura, T.; Wskatsuki, Y. *Organometallics* **1997**, *16*, 2963.

(18) Shannon, R. D. *Acta Crystallogr. Sect. A* **1976**, *32*, 751.

Table 1. Selected Bond Distances (Å) and Angles (deg) for Complex 1

Bond Distances			
Sm1−N1	2.374(3)	Sm1−N2	2.377(3)
Sm1−C1	2.844(3)	Sm1−C2	2.783(3)
Sm1−C3	2.716(3)	Sm1−C4	2.729(3)
Sm1−C5	2.776(3)	Sm1−C7	2.815(3)
Sm1−C8	2.813(3)	Sm1−C9	2.763(3)
Sm1−C10	2.729(3)	Sm1−C11	2.741(3)
Na1−O1	2.298(4)	Na1−O2	2.291(4)
Na1−C1	2.974(3)	Na1−C2	2.819(3)
Na1−C3	2.745(3)	Na1−C4	2.817(3)
Na1−C5	2.978(3)	Na1−C7a	2.902(3)
Na1−C8a	2.968(3)	Na1−C9a	2.917(3)
Na1−C10a	2.803(3)	Na1−C11a	2.801(3)
Na1−Cent(1)[a]	2.609	Na1−Cent(2)[b]	2.621
Sm1−Cent(1)	2.501	Sm1−Cent(2)	2.503
Angles			
N1−Sm1−N2	102.43(13)	Cent(1)−Sm1−Cent(2)	122.7
O1−Na1−O2	95.78(19)	Cent(1)−Na1−Cent(2)	125.1

[a] Cent(1) is the centroid of the C(1)−C(5) ring. [b] Cent(2) is the centroid of the C(7)−C(11) ring.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Complex 2

Bond Distances			
Er−N1	2.286(6)	Er−N2	2.288(6)
Er−C1	2.730(6)	Er−C2	2.687(6)
Er−C3	2.645(8)	Er−C4	2.669(8)
Er−C5	2.742(6)	Er−C7	2.699(7)
Er−C8	2.646(7)	Er−C9	2.664(7)
Er−C10	2.712(7)	Er−C11	2.752(8)
Na−O1	2.287(7)	Na−O2	2.296(6)
Na−C1a	2.962(8)	Na−C2a	2.903(7)
Na−C3a	2.800(7)	Na−C4a	2.804(8)
Na−C5a	2.886(8)	Na−C7	2.811(8)
Na−C8	2.741(8)	Na−C9	2.806(8)
Na−C10	2.969(8)	Na−C11	2.965(8)
Na−Cent(1)[a]	2.613	Na−Cent(2)[b]	2.603
Er−Cent(1)	2.417	Er−Cent(2)	2.421
Angles			
N1−Er−N2	102.3(2)	Cent(1)−Er−Cent(2)	123.8
O1−Na−O2	96.6(3)	Cent(1)−Na−Cent(2)	125.9

[a] Cent(1) is the centroid of the C(1)−C(5) ring. [b] Cent(2) is the centroid of the C(7)−C(11) ring.

Table 3. Experimental Data for the X-ray Diffraction Study of Complexes 1 and 2

	1	2
formula	$C_{44}H_{50}N_2O_2NaSm$	$C_{44}H_{50}N_2O_2NaEr$
fw	812.20	829.11
temp (K)	294(2)	296(2)
wavelength (Å)	0.71073	0.71073
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$ (No. 14)	$P2_1/n$
a (Å)	9.006(1)	8.889(2)
b (Å)	22.009(2)	21.982(4)
c (Å)	20.763(2)	20.646(3)
β (deg)	101.83(1)	101.300(10)
V (Å^3)	4028.1(5)	3956.0(13)
Z	4	4
D (calcd) (Mg/m^3)	1.339	1.392
abs coeff (mm^{-1})	1.505	2.170
F(000)	1668	1692
cryst size (mm)	0.35 × 0.40 × 0.80	0.60 × 0.44 × 0.12
θ range for data collecn (deg)	1.36−25.57	2.21−25.01
limiting indices	$-10 \le h \le 10$, $-26 \le k \le 26$, $-25 \le l \le 0$	$0 \le h \le 10$, $0 \le k \le 26$, $-24 \le l \le 24$
no. of reflns collected	12 175	7934
no. of indep reflns	6665 (R(int) = 0.0565)	6351(R(int) = 0.0368)
max. and min. transmission	1.093 and 0.915	0.7808 and 0.3560
no. of data/restraints/params	6665/393/452	6351/0/453
goodness-of-fit on F^2	1.109	0.899
final R indices ($I > 2\sigma(I)$)	R1 = 0.0555 wR2 = 0.1393	R1 = 0.0436 wR2 = 0.0845
R indices (all data)	R1 = 0.0603 wR2 = 0.1438	R1 = 0.0851 wR2 = 0.0931
largest diff peak and hole (e Å^{-3})	0.725 and −0.857	0.821 and −0.890

for **2**) can be compared to the 2.924 Å observed in the zigzag chain polymer $[C_5H_5Na(tmeda)]_n$[19] and the 2.83 Å in $[NaYb(C_5H_5)_3]$.[14]

Experimental Section

All manipulations were carried out under an argon atmosphere using standard Schlenk techniques. Tetrahydrofuran (THF) and toluene were dried and freed of oxygen by refluxing over sodium/benzophenone ketyl and distilled under argon prior to use. $NaNPh_2$ was prepared as reported in the literature.[13]

Lanthanide metal analyses were carried out by complexometric titration, and sodium content was determined by using ICP-AES technology. Carbon, hydrogen, and nitrogen analyses were performed by direct combustion. The IR spectra were obtained on a Magna-550 spectrometer.

$[Na(THF)_2(\mu\text{-}\eta^5{:}\eta^5\text{-}MeC_5H_4)_2Sm(NPh_2)_2]_n$, 1. To a slurry of $SmCl_3$ (2.13 g, 8.3 mmol) in 20 mL of THF was added 16.7 mL of a solution MeC_5H_4Na (16.6 mmol) in THF. The mixture was stirred at room temperature for 48 h. After centrifugation, the solution of $(MeC_5H_4)_2SmCl$ (43.5 mL, 4.98 mmol) was cooled to 0 °C, and a solution of $NaNPh_2$ (8.4 mL, 4.98 mmol) in THF was added. The mixture was stirred 48 h at room temperature. After centrifugation, the THF was completely removed, and about 5 mL of toluene was added. The turbid solution became clear, and orange crystals were formed when some THF was added. Yield: 1.3 g (32.5%). Using 2 equiv of $NaNPh_2$ in this reaction afforded **1** in a high yield (63%). Mp (sealed): 114 °C (dec). Anal. Calcd for $C_{44}H_{50}N_2O_2NaSm$: C, 65.06; H, 6.20; N, 3.45; Na, 2.83; Sm, 18.51. Found: C, 64.63; H, 5.96; N, 3.41; Na, 2.74; Sm, 18.55. IR (KBr pellet,cm^{-1}): 3044(w), 2971(w), 1593(s), 1493(s), 1416(w), 1312(m), 1246(w), 1173(w), 1080(w), 1026(w), 876(w), 748(s), 691(m), 502(w).

$[Na(THF)_2(\mu\text{-}\eta^5{:}\eta^5\text{-}MeC_5H_4)_2Er(NPh_2)_2]_n$, 2. This complex was prepared from the reaction of $(MeC_5H_4)_2ErCl$ (25 mL, 3.38 mmol) with $NaNPh_2$ (12.1 mL, 6.76 mmol) in THF using the procedure described above. Pink crystals were obtained. Yield: 2.23 g (79.5%). Mp (sealed): 125 °C (dec). Anal. Calcd for $C_{44}H_{50}N_2O_2NaEr$: C, 63.74; H, 6.08; N, 3.40; Na, 2.77; Er, 20.17. Found: C, 63.28; H, 5.71; N, 3.28; Na, 2.35; Er, 20.68. IR (KBr pellet,cm^{-1}): 3044(w), 2971(w), 1597(s), 1493(s), 1416(w), 1316(m), 1219(s), 1157(s), 1080(w), 1026(w), 876(w), 748(s), 691(m), 505(m).

X-ray Crystallographic Studies. Suitable crystals were selected and mounted in thin-walled glass capillaries for X-ray structure analysis. Reflections were collected at room temperature on a Rigaku RAXIS IIc imaging-plate diffractometer for **1** and a Siemens P4 diffractometer for **2** using graphite-monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation. During the course of collection of the intensity data no significant decays were observed. Data were corrected for Lorentz and polarization effects and empirical absorption. A summary of crystallographic data is given in Table 3.

The crystal structures were solved by direct methods, and refinements on F^2 were carried out by full-matrix least-squares

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(19) Aoyagi, T.; Shearer, H. M. M.; Wade, K.; Whitehead, G. *J. Organomet. Chem.* **1979**, *175*, 21.

analysis. Anisotropic temperature parameters were considered for all non-hydrogen atoms, while hydrogen atoms were included in calculated positions. All calculations were carried out using the SHELX-97 program.[20]

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Supporting Information Available: Details of structure determinations of complexes **1** and **2**, including final coordinates, thermal parameters, bond distances, and bond angles are available free of charge via the Internet at http:/pubs.acs.org.

OM9906215

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[20] Sheldrick, G. M. *SHELX-97*, Package for Crystal Structure Solution and Refinement; University of Gottingen: Germany, 1997.