Metallomacrocycle Complexes of Lanthanides with Bridged Amide Ligands: Syntheses and Molecular Structures of $[\{\mu_2\text{-}p\text{-}(Me_3SiN)_2C_6H_4\}YbCl(THF)_2]_2$ and $[\{\mu_2\text{-}p\text{-}(Me_3SiN)_2C_6H_4\}Nd(\mu_2\text{-}Cl)(THF)]_4$ 2PhMe

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*Summary: Reactions of anhydrous $YbCl_3$ and $NdCl_3$ with dilithium N,N′-di(trimethylsilyl)-p-benzenediamide in THF in 1:1 molar ratio afforded a cyclic binuclear complex of Yb, $[\{\mu_2\text{-}p\text{-}(Me_3SiN)_2C_6H_4\}YbCl(THF)_2]_2$ (**1**), and a cyclic tetranuclear complex of Nd, $[\{\mu_2\text{-}p\text{-}(Me_3SiN)_2C_6H_4\}Nd(\mu_2\text{-}Cl)(THF)]_4\cdot$ 2PhMe (2), respectively, in good isolated yields. **1** is a hexagon consisting of two Yb atoms and four nitrogen atoms from two bridged diamides, while **2** is a cage-like macrocycle formed via assembly by weak bonding of Nd−C (aromatic carbon), in which each Nd atom is coordinated to two nitrogen atoms from two linked diamide ligands, respectively, two bridged chlorine atoms, and one oxygen atom of THF, additionally, interacting with the three aromatic carbons from two phenyl groups, respectively.*

Supramolecular chemistry has attracted much attention in the last decades, as supramolecular systems can be widely used in molecule recognition,[1] selective transformations,[2] translocation of drugs across membranes,[3] and construction of macroscopic architectures and devices on the molecular level.[4] Metallomacrocycles are the important building blocks in modern supramolecules owing to their potential applications in functional materials. Therefore, the synthesis of metallomacrocycles with specific frameworks has received a great deal of attention.[5]

Amide ligands, as an alternative to the cyclopentadienyl anion,[6] have been used extensively in organolanthanide chemistry, as their electronic and steric environment can easily be modified by the substituent variation on the nitrogen atoms, and these amide complexes show highly catalytic activity in hydroamination/cyclyzation,[7] hydrosilylation,[8] Tischenko reaction,[9] and the polymerization of polar monomers as well.[10] Moreover, the bridged bidentate and polydentate amide ligands

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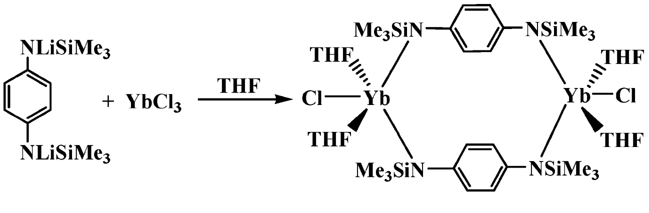
Scheme 1



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also have potential in the formation of supramolecular systems and metallomacrocycles.[11] However, the metallomacrocycle of lanthanides supported by linked diamide anions was scarcely reported. Recently, we tried to synthesize metallomacrocycles of lanthanides supported by *N*,*N*′-di(trimethylsilyl)-*p*-benzenediamine ligands and to further understand their chemical behavior. The results indicated that the two novel metallomacrocyclic complexes of lanthanides, cyclic binuclear ytterbium complex $[\{\mu_2\text{-}p\text{-}(Me_3SiN)_2C_6H_4\}YbCl(THF)_2]_2$ (**1**) and cyclic tetranuclear neodymium complex $[\{\mu_2\text{-}p\text{-}(Me_3SiN)_2C_6H_4\}Nd(\mu_2\text{-}Cl)(THF)]_4 \cdot 2PhMe$ (**2**), can be successfully isolated via assembly in high yield. Herein we report the results.

Results and Discussion

Lanthanide metal to aromatic carbon bonding interactions are often present in lanthanide complexes with aromatic amide ligands[12] as well as phenoxo ligands.[13] The presence of such interactions may provide an opportunity to make the bidentate diamide ligand a formal polydentate that is favorable for the formation of metallomacrocycle. Taking the above into consideration, the bridged diamide with rigid phenyl group *N*,*N*′-di(trimethylsilyl)-*p*-benzenediamine (LH_2) was chosen as the ligand precoursor. The LH_2 was synthesized by the reaction of *p*-benzenediamine with Me_3SiCl according to the published method.[14] The dilithium salt LLi_2 was synthesized in situ by the reaction of *N*,*N*′-di(trimethylsilyl)-*p*-benzenediamine with *n*-butyllithium in 1:2 molar ratio. The metathesis reaction of anhydrous $YbCl_3$ with in situ generated LLi_2 in 1:1 molar ratio at room temperature in THF went smoothly, and after workup a novel metallomacrocycle of Yb (**1**) was isolated as orange-red microcrystals in moderate yield (Scheme 1).

Complex **1** was first characterized by elemental analysis and IR spectroscopy. The ^1H NMR data are not usable, due to the strong paramagnetic nature of ytterbium. The further determination of its molecular structure was carried out by X-ray diffraction technique.

The same reaction with $NdCl_3$ yielded a novel complex of Nd (**2**) as blue-green crystals in 67% yield. X-ray crystal structural analysis indicated **2** to be a tetranuclear metallomacrocycle (Scheme 2). Its ^1H NMR spectra are not resolvable, due to the strong paramagnetic nature of the Nd ion.

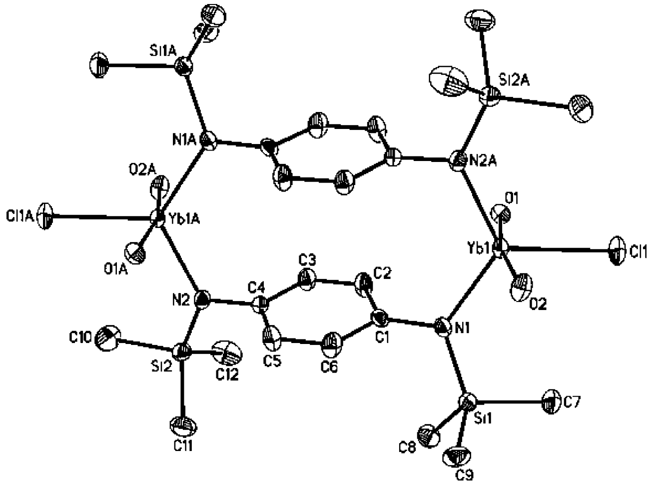


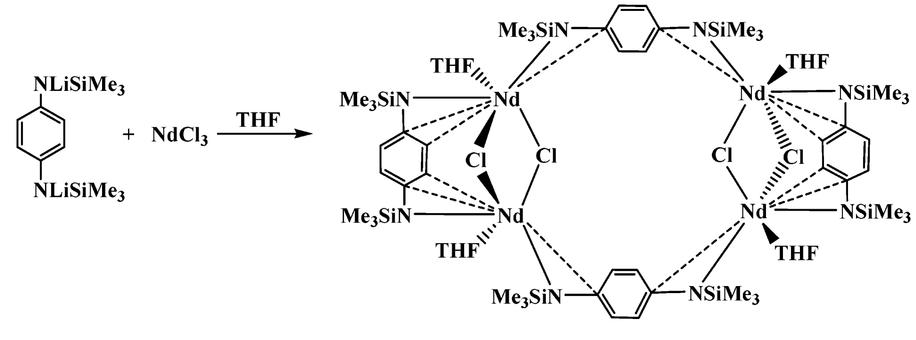
Figure 1. ORTEP diagram of $[\{\mu_2\text{-}p\text{-}(Me_3SiN)_2C_6H_4\}YbCl(THF)_2]_2$ (**1**). C and H atoms in THF are omitted for clarity.

Both complexes are moderately air- and moisture-sensitive, but thermally stable. They are freely soluble in donor solvents, such as THF and DME, moderately soluble in toluene and benzene, and slightly soluble in hexane.

Crystals of **1** and **2** suitable for X-ray diffraction were grown from toluene at 0 °C and room temperature, respectively. ORTEP diagrams depicting the molecular structures of **1** and **2** are shown in Figures 1 and 2, respectively. Detailed crystal and structural refinement data are listed in Table 1. Selected bond lengths and angles are given in Table 2 for **1** and Table 3 for **2**.

As shown in Figure 1, complex **1** is a centrosymmetrical distorted hexagon formed from two Yb atoms and four nitrogen atoms from linked di(silylamide) moieties. The coordination geometry around each ytterbium center is equivalent. Each metal center of Yb is coordinated to two nitrogen atoms from two linked diamide groups, one chlorine, and two oxygen atoms from two THF molecules with angles of N(1)−Yb−N(2A), 120.1(2)°; N(1)−Yb−Cl(1), 121.6(2)°; N(2A)−Yb−Cl(1), 118.2(2)°; and O(1)−Yb−O(2), 168.5(2)°. Thus, the coordination geometry around each Yb can be best described as a distorted trigonal bipyramid with a chelating diamide and a chlorine atom in the equatorial plane and two THF molecules in each axial position. The two aromatic rings are parallel to each other. To our best knowledge, this is the first hexagonal structure of a metallomacrocycle of ytterbium with amide as an anion. The bond lengths of Yb(1)−N(1) (2.174(6) Å) and Yb(1)−N(2A)

Scheme 2



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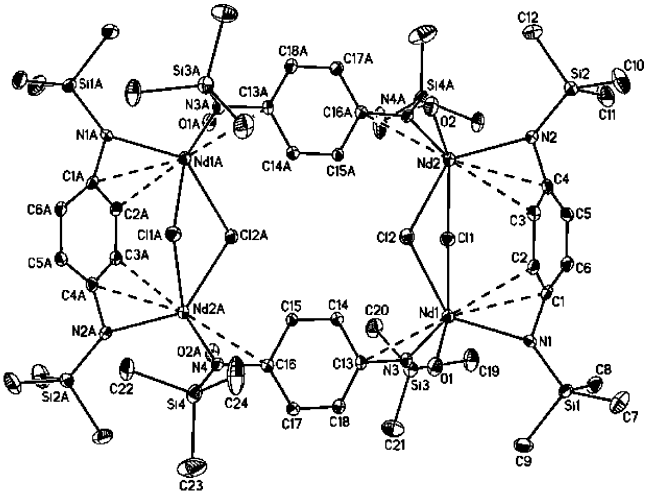

Figure 2. ORTEP diagram of [{μ_2-*p*-$(Me_3SiN)_2C_6H_4$}Nd(μ_2-Cl)-(THF)]$_4$·2PhMe (**2**). C and H atoms in THF are omitted for clarity.

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

	1	2
empirical formula	$C_{40}H_{76}Cl_2N_4O_4Si_4Yb_2$	$C_{78}H_{136}Cl_4N_8O_4Si_8Nd_4$
fw	1206.39	2193.43
temp (K)	193(2)	193(2)
wavelength (Å)	0.7107	0.7107
cryst syst	monoclinic	triclinic
space group	*C*2/*c*	$P\bar{1}$
unit cell dimens		
a (Å)	25.127(3)	13.827(2)
b (Å)	12.084(1)	14.237(1)
c (Å)	17.464(2)	14.796(1)
α (deg)	90	61.759(5)
β (deg)	93.48(3)	85.629(9)
γ (deg)	90	86.579(9)
V (Å^3)	5293.0(10)	2557.7(4)
Z	4	1
D_{calc} (g cm^{-3})	1.514	1.424
F(0 0 0)	2424	1112
abs coeff (mm^{-1})	3.742	2.239
θ range for data collection (deg)	3.03−27.48	3.03−25.35
no. of reflns collected	28 590	25 563
no. of indep reflns	6069	9305
no. of data/restraints/ params	6069/3/260	9305/20/476
final *R*[$I > 2\sigma(I)$]	0.0561	0.0492
R_w	0.1299	0.0995
goodness-of-fit on F^2	1.232	1.129
largest diff peak and hole (e A^{-3})	2.332, −2.741	1.687, −0.693

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complex 1

Bond Lengths			
Yb(1)−N(1)	2.174(6)	N(1)−C(1)	1.432(8)
Yb(1)−N(2A)	2.173(6)	N(2)−C(4)	1.440(8)
Yb(1)−Cl(1)	2.536(2)	Yb(1)−C(4A)	3.031(6)
Yb(1)−O(1)	2.306(4)	Yb(1)−C(1)	3.144(6)
Yb(1)−O(2)	2.292(5)		
Bond Angles			
N(1)−Yb(1)−N(2A)	120.1(2)	O(1)−Yb(1)−O(2)	169.5(2)
N(2A)−Yb(1)−Cl(1)	118.2(2)	C(1)−N(1)−Yb(1)	120.0(4)
N(1)−Yb(1)−Cl(1)	121.6(2)	C(4)−N(2)−Yb(1A)	112.5(4)

(2.173(6) Å) are in the range of normal distances of the Yb−N *σ* bond. The values are identical to those in $[(Me_3Si)_2N]_2$Yb-(μ-Cl)(THF)]$_2$ (2.174(5) and 2.198(5) Å)[15] and [{$(Me_3Si)_2$NYb-(μ'-Cl)$_2$Li(THF)$_2$}(μ-Cl)]$_2$ (2.199(4) Å).[16] The Yb(1)−Cl(1) bond length of 2.536(2) Å is normal.[17] The Yb(1)−C(1, 4A) distances are quite long, and it is suggested that the *π* contribution of the aromatic rings to the Yb ion is negligible.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Complex 2

Bond Lengths			
Nd(1)−N(1)	2.328(5)	Nd(2)−N(2)	2.322(5)
Nd(1)−N(3)	2.265(5)	Nd(2)−N(4A)	2.275(5)
Nd(1)−Cl(1)	2.789(2)	Nd(2)−Cl(1)	2.803(2)
Nd(1)−Cl(2)	2.867(2)	Nd(2)−Cl(2)	2.859(2)
Nd(1)−O(1)	2.464(4)	Nd(2)−O(2)	2.470(4)
Nd(1)−C(1)	2.755(6)	Nd(2)−C(4)	2.775(6)
Nd(1)−C(2)	2.925(6)	Nd(2)−C(3)	2.994(6)
Nd(1)−C(13)	2.875(6)	Nd(2)−C(16A)	2.957(6)
Bond Angles			
N(3)−Nd(1)−N(1)	109.5(2)	N(4A)−Nd(2)−N(2)	112.8(2)
N(3)−Nd(1)−Cl(2)	124.8(1)	N(4A)−Nd(2)−Cl(2)	124.6(1)
N(1)−Nd(1)−Cl(2)	125.7(1)	N(2)−Nd(2)−Cl(2)	122.7(1)
O(1)−Nd(1)−Cl(1)	158.1(1)	O(2)−Nd(2)−Cl(1)	157.4(1)
C(1)−N(1)−Nd(1)	91.9(3)	C(4)−N(2)−Nd(2)	92.8(3)
C(13)−N(3)−Nd(1)	100.0(3)	C(16A)−N(4A)−Nd(2)	104.0(3)
Nd(1)−Cl(1)−Nd(2)	100.0(5)	Nd(1)−Cl(2)−Nd(2)	96.9(5)
Torsion Angles			
C(2)−C(1)−C(6)−C(5)	−9.5(9)	C(13)−C(14)−C(15)−C(16)	−4.6(9)
C(3)−C(4)−C(5)−C(6)	9.1(9)	C(14)−C(15)−C(16)−C(17)	4.5(9)

Complex **2** possesses a cage-like structure that results from the coordination of eight nitrogen atoms from four linked diamide ligands to four neodymium atoms, respectively (Figure 2). **2** is also centrosymmetrical. Each Nd atom is ligated by two nitrogen atoms from two linked di(silylamine) moieties, two asymmetrically bridged chlorine atoms, and one oxygen atom of a THF molecule. The coordinate geometry around each Nd atom can be described as a distorted trigonal bipyramid with the THF oxygen atom and one of the bridged chlorines (Cl(1)) apical and the two nitrogen atoms and the other bridged chlorine (Cl(2)) equatorial. The angles among Nd and the axial atoms are 158.1(1)° for Nd(1) and 157.4(1)° for Nd(2), which deviate greatly from 180°. Considerable variation in the equatorial angles, 112.8(2)−124.6(1)° for Nd(1) and 109.5(2)−125.7(1)° for Nd(2), was also observed, although the sum of these angles is 360°. It was noticed that the distances of Nd to C_{ipso} and Nd to C_{ortho} are 2.755(6) Å (Nd(1)−C(1)), 2.775(6) Å (Nd(2)−C(4)), 2.875(6) Å (Nd(1)−C(13)), 2.957(6) Å (Nd(2)−C(16A)) (average Nd−C_{ipso} 2.841 Å), and 2.925(6) Å (Nd(1)−C(2)), 2.994(6) Å (Nd(2)−C(3)) (average Nd−C_{ortho} 2.960 Å), respectively. Such short distances and the small Nd−N−C_{ipso} angles (mean bond angles 97.2(3)°) suggested the presence of Nd−C (aromatic carbon) bonds. The average distances are in the same range as those observed in the other known complexes of

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lanthanide metal−π-arene interactions. The values can be compared with 2.93(3) and 3.04 Å observed for the average Nd−C distances found in (η-C_6H_6)Nd($AlCl_4$)$_3$[18] and Nd_2(O-2,6-*i*-$Pr_2C_6H_3$)$_6$,[19] respectively. The data are also comparable to the Y−C_{ipso} (average 2.75 Å) and Y−C_{ortho} (average 2.87 Å) distances observed in {[6,6′-Me_2-(C_6H_3)$_2$](2,2′-$NSiMe_2{}^t$-Bu)$_2$}YCl(THF)$_2$ supported by the chelating diamide ligands.[12] It is obvious that the presence of interactions of Nd with three aromatic carbons from two phenyl rings leads to the formation of a cage-like structure, in which the linked diamide plays the role of polydentate ligand. To our best knowledge, this is the first example of the formation of a metallomacrocycle through weak bonds such as metal to aromatic carbon interaction. The interaction between Nd and aromatic carbons results in the distortion of two phenyl rings. The torsion angles are −9.5(9)° for C(2)−C(1)−C(6)−C(5), 9.1(9)° for C(3)−C(4)−C(5)−C(6), −4.6(9)° for C(13)−C(14)−C(15)−C(16), and 4.5(9)° for C(14)−C(15)−C(16)−C(17). The Nd−μ-Cl bond distances are 2.789(2), 2.867(2), 2.803(2), and 2.859(2) Å with an average distance of 2.830(2) Å, which is in the range found in other complexes with a bridged Nd−μ-Cl bond.[16]

Conclusion

Two new metallomacrocycles of lanthanides supported by linked di(silylamide) ligands, [{μ_2-*p*-(Me_3SiN)$_2C_6H_4$}YbCl-(THF)$_2$]$_2$ (**1**) and [{μ_2-*p*-(Me_3SiN)$_2C_6H_4$}Nd(μ_2-Cl)(THF)]$_4$·2PhMe (**2**), were synthesized by assembly and structurally characterized. The interactions of Nd−π-C (aromatic carbons) led to the formation of a cage-like structure. Further studies on the chemical behavior of these complexes and the synthesis of metallomacrocycles are proceeding.

Experimental Section

General Procedures. All manipulations were performed under pure argon with rigorous exclusion of air and moisture using standard Schlenk techniques. Solvents were degassed and distilled from sodium benzophenone ketyl under argon prior to use. Anhydrous $LnCl_3$[20] and *p*-(Me_3SiNH)$_2C_6H_4$[14] were prepared according to the reported procedures. Melting points were determined in argon-filled capillary tubes and are uncorrected. Lanthanide metal analyses were carried out by complexometric titration. Carbon, hydrogen, and nitrogen analyses were performed by direct combustion on a Carlo-Erba EA-1110 instrument; quoted data are the average of at least two independent determinations. The IR spectra were recorded with a Nicolet Magna-IR 550 spectrometer.

Synthesis of [{μ_2-*p*-(Me_3SiN)$_2C_6H_4$}YbCl(THF)$_2$]$_2$ (1). A Schlenk flask was charged with *p*-(Me_3SiNH)$_2C_6H_4$ (0.50 g, 1.98 mmol), THF (10 mL), and a stir bar. The solution was cooled to 0 °C, and ^nBuLi (2.77 mL, 3.96 mmol, 1.43 M in hexane) was added. The solution was slowly warmed to room temperature and stirred for 1 h and then added slowly to a pale gray slurry of $YbCl_3$ (0.55 g, 1.98 mmol) in 20 mL of THF. The color of the reaction solution gradually changed to red. The reaction mixture was then stirred for 48 h at room temperature. The solvent was removed in vacuo, the residue was extracted with toluene, and LiCl was removed by centrifugation. After the extracts were concentrated, orange-red crystals of **1** (0.66 g, 56%) were obtained at 0 °C for 2 days. Mp: 167−169 °C (dec). Anal. Calc for $C_{40}H_{76}Cl_2N_4O_4Si_4Yb_2$: C 39.79, H 6.30, N 4.64, Yb 29.02. Found: C 39.84, H 6.29, N 4.62, Yb 28.69. IR (KBr pellet, cm^{-1}): 3210 (s), 1616 (m), 1509 (s), 1403 (s), 1301 (m), 1257 (m), 833 (m).

Synthesis of [{μ_2-*p*-(Me_3SiN)$_2C_6H_4$}Nd(μ_2-Cl)(THF)]$_4$·2PhMe (2). A Schlenk flask was charged with *p*-(Me_3SiNH)$_2C_6H_4$ (0.50 g, 1.98 mmol), THF (10 mL), and a stir bar. The solution was cooled to 0 °C, and ^nBuLi (2.77 mL, 3.96 mmol, 1.43 M in hexane) was added. The solution was slowly warmed to room temperature and stirred for 1 h and then added slowly to a pale gray slurry of 1.98 mmol of $NdCl_3$ (0.49 g) in 20 mL of THF. The color of the reaction solution gradually changed to blue-green. The reaction mixture was then stirred for 48 h at room temperature. The solvent was removed in vacuo, the residue was extracted with toluene, and LiCl was removed by centrifugation. After the extracts were concentrated, blue-green crystals of **2** (0.73 g, 67%) were obtained at room temperature for 1 day. Mp: 124−125 °C (dec). Anal. Calc for $C_{64}H_{120}Cl_4N_8O_4Si_8Nd_4$: C 37.50, H 5.86, N 5.47, Nd 28.16. Found: C 37.77, H 5.98, N 5.19, Nd 27.83. IR (KBr pellet, cm^{-1}): 3200 (m), 1618 (m), 1512 (s), 1403 (m), 1300 (m), 1257 (m), 833 (m).

X-ray Crystallography. Suitable single crystals of complexes **1** and **2** were sealed in thin-walled glass capillaries filled under argon for single-crystal structure determination. Intensity data for **1** and **2** were collected at low temperature on a Rigaku Mercury CCD with graphite-monochromated Mo Kα radiation. The crystal structure was solved by direct methods and expanded by Fourier techniques. Atomic coordinates and thermal parameters were refined by full-matrix least-squares procedures based on $|F|^2$. All non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were treated as idealized contributions. The structures were solved and refined using the SHELXL-97 programs.

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Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

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