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双胺配体$[K_2(L)(THF)_2]$(L=$[Ph_2Si(NAr)_2]^{2-}$, Ar=2,6-^{i}Pr$_2$C$_6$H$_3$)构筑的两个低价稀土镱化合物

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摘要:以双胺类配体$[K_2(L)(THF)_2]$ (**1**)(L=$[Ph_2Si(NAr)_2]^{2-}$, Ar=2,6-^{i}Pr$_2$C$_6$H$_3$)与二价稀土 $YbI_2(THF)_2$ 的交换反应得到 2 个不同类型的化合物$[Yb(L)(THF)_3]$ (**2**)和$\{Yb(L)_2[K(THF)_2]_2\}$ (**3**)。对化合物进行 X-射线单晶结构解析,核磁共振和元素分析表征。研究结果表明:化合物 **2** 中,通过 1 个双齿含氮配体和 3 个中性 THF 分子配位,以五配位模式稳定二价镱稀土中心。而化合物 **3** 中二价稀土镱是与 2 个螯合胺类配体配位,以共平面、四配位模式稳定其金属中心。K^+恰好在配体的 2 个苯环之间,形成独特的三明治结构,有助于化合物的稳定。

关键词:稀土化学;胺基配体;镱

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Two Divalent Ytterbium Complexes with Diamido Ligands $[K_2(L)(THF)_2]$(L=$[Ph_2Si(NAr)_2]^{2-}$, Ar=2,6-^{i}Pr$_2$C$_6$H$_3$)

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Abstract: The reaction of diamido ligand $[K_2(L)(THF)_2]$ (**1**) (L=$[Ph_2Si(NAr)_2]^{2-}$, Ar=2,6-^{i}Pr$_2$C$_6$H$_3$) with $YbI_2(THF)_2$ afforded two complexes $[Yb(L)(THF)_3]$ (**2**) and $\{Yb(L)_2[K(THF)_2]_2\}$ (**3**), which were characterized by X-ray structure analysis, NMR and elemental analysis. The coordination geometry of complex **2** is five-coordinated, and Yb metal center is coordinated by one amido ligand and three THF molecules. Complex **3** adopts a four-coordinated, nearly planar geometry around the Yb(Ⅱ) center. Two potassium ion is sandwiched between two phenyl rings via cation-arene π-interactions, which helps to stabilize the metal center. CCDC: 689221, **2**; 689222, **3**.

Key words: lanthanide chemistry; amido ligand; ytterbium

In the past decades, there has been a growing interest in the chemistry of organolanthanide complexes supported by various non-cyclopentadienyl ligands[1-3]. Nitrogen donors are commonly used to support lanthanide metals, and the significance of sterically encumbered amido ligands was first demonstrated in the successfully isolation of lanthanide (Ⅲ) complex $\{Ln[N(SiMe_3)_2]_3\}$, as exemplified by the pioneering work of Bradley and co-workers[4-5]. In the past years, there has been increasing interest in the development

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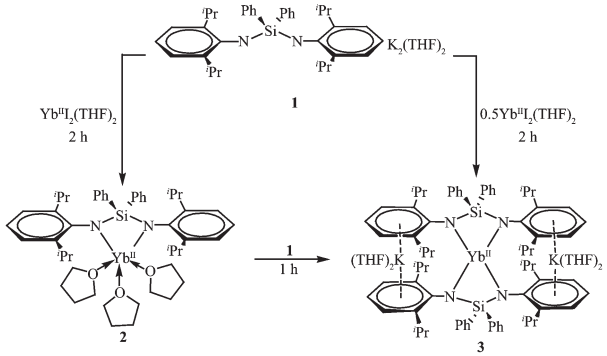
of various amido ligands that have been widely used to stabilize lanthanide(Ⅱ) metals such as {NaLn[N(SiMe$_3$)$_2$]$_3$} (Ln=Yb, Eu) and rich chemistry has been demonstrated in terms of structures and reactivity[6-9]. Besides these three traditional lanthanide(Ⅱ) (Sm, Eu and Yb) ions, it has also been shown that a reaction system with the [N(SiMe$_3$)$_2$]$^-$ ligand and the more reducing Tm(Ⅱ), Dy(Ⅱ) and Nd(Ⅱ) ions has led to a facile reduction of N_2 and the isolation of the corresponding $(N_2)^{2-}$ complexes[10-11]. Generally speaking, divalent lanthanide complexes with high reactive metal centers are very difficult to prepare. Thus the synthesis of a wide variety of lanthanide amido complexes remains an important work.

Chemical properties are always affected to some extent by the steric and electronic environment of the metal center. Therefore, to synthesize low-valent lanthanide complexes, the highly reducing nature of metal centers and their large ionic radii require that special care must be taken in the choice of the ligand with its proper steric bulk surrounded by the stabilization of lanthanide(Ⅱ) and reaction conditions to prevent unexpected results[12]. In recent years, N,N′-chelating β-diketiminates [(R^{1}NCR^2)$_2$CR^3]$^-$ (nacnac$^-$)[13] and guanidinate ligands [(ArN)$_2$CN(C$_6$H$_{11}$)$_2$]$^-$ (Giso$^-$)[14-15] have been utilized in the preparation and characterization of homoleptic four-coordinate Ln(Ⅱ) (Yb and Sm) complexes. In addition, Prof. Lee group reported divalent lanthanide complexes supported by a bulky 2-pyridyl amido and unsymmetrical benzamidinate ligands, which were very interesting[16-17].

In our previous work, we directly obtained planar four-coordinate Ln(Ⅱ) diamido complexes {Ln(L)$_2$[K(solv.)$_x$]$_2$} (Ln=Sm and Eu), which represent the first example of lanthanide bearing heteroleptic sandwich structures[18-21]. These results inspired us to extend the coordination chemistry of bulky diamido ligands to ytterbium(Ⅱ) by taking advantage of related synthetic routes. We have explored the coordination of amido ligand H$_2$L (L=[Ph$_2$Si(NAr)$_2$]$^{2-}$, Ar=2,6-^{i}Pr$_2$C$_6$H$_3$)[22] to stabilize the ytterbium(Ⅱ) complex, {Yb(L)$_2$[K(THF)$_2$]$_2$} (**3**), by the reaction of [Yb(L)(THF)$_3$] (**2**) and one eqivement of [K$_2$(L)(THF)$_2$] (**1**)[18], as shown in Scheme 1. Herein, we reported the synthesis and structural studies of these complexes. According to our experimental results, it was difficult to isolate monometallic complex **2**, and easy to obtain heterotrimetallic sandwich complex **3**. To the best of our knowledge, homoleptic and heterotrimetallic divalent ytterbium complexes with diamido ligands are meaningful in the lanthanide chemistry.



Scheme 1

1 Experimental

1.1 Materials and methods

All procedures were performed under vacuum using standard Schlenk techniques or in a nitrogen-filled drybox. THF was pretreated with KOH and was then distilled from sodium benzophenone ketyl prior to use. Hexane and toluene were purified by distillation from sodium/triglyme benzophenone ketyl or CaH$_2$. All other commercially available chemicals were used after appropriate purification. NMR spectra were recorded on a Bruker DPX 300 spectrometer. Elemental analyses (C, H, N) were carried out in the microanalytical laboratory of Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences.

1.2 Synthesis of compounds

Synthesis of [Yb(L)(THF)$_3$] (**2**). A solution of [K$_2$(L)(THF)$_2$] (1.15 g, 1.5 mmol) in THF (15 mL) was treated with YbI$_2$(THF)$_2$ (0.84 g, 1.5 mmol) at room temperature to give the title compound **2** as red crystals (0.70 g, 49.5 %). ^{1}H NMR (C$_6$D$_6$, 300 MHz): δ 7.62 (d, J=4.8 Hz, 4H, ArH), 7.11~7.21 (m, 10H, ArH), 6.93 (t, J=7.2 Hz, 2H, ArH), 3.26~3.52 (m, 12H, THF), 4.33 (sept, J=6.9 Hz, 4H, CHMe$_2$), 1.25~1.45 (br, 12H, THF), 1.11 (d, J=6.9 Hz, 24H, CHMe$_2$). ^{13}C NMR (C$_6$D$_6$,

75.47 MHz): δ 159.3, 154.7, 148.6, 142.9, 135.8, 126.8, 124.9, 116.4 (Ar), 69.1, 28.2 (OCH_2CH_2 (THF)), 25.7, 23.9 ($CHMe_2$). Anal. Calcd. for $C_{48}H_{68}N_2O_3SiYb$(%): C, 62.52; H, 7.43; N, 3.04. Found(%): C, 62.59; H, 7.38; N, 3.32.

Synthesis of {Yb(L)$_2$[K(THF)$_2$]$_2$} (**3**). A green suspension of YbI_2(THF)$_2$ (0.59 g, 1 mmol) in THF was added to a solution of [K_2(L)(THF)$_2$] (1.54 g, 2 mmol) to give the compound **3** as green crystals (0.79 g, 45.0%). ^{1}H NMR (C_6D_6, 300 MHz): δ 7.71 (d, J=3 Hz, 8H, ArH), 7.12~7.16 (m, 12H, ArH), 7.08 (s, 12H, ArH), 3.56 (br, 16H, THF), 3.39 (sept, J=6.6 Hz, 8H, $CHMe_2$) 1.43 (br, 16H, THF), 1.00 (d, J=6.6 Hz, 48H, $CHMe_2$). ^{13}C NMR (C_6D_6, 75.47 MHz): δ 143.1, 139.8, 135.8, 130.4, 124.1, 123.4 (Ar), 68.1, 66.2, 29.4, (OCH_2CH_2(THF)), 26.1, 23.9, 22.9, 15.9($ArCHMe_2$). Anal. Calcd. for $C_{80}H_{104}K_2N_4O_2Si_2Yb$ (**3**·2THF)(%): C, 65.76; H, 7.17; N, 3.83. Found(%): C, 65.38; H, 7.31; N, 3.94.

1.3 Crystal structure determination

X-ray crystallographic data of **2** and **3** were collected under polybutenes, isobutylene oil at room temperature. All measurements were made on a Bruker Smart Apex CCD diffractometer with graphite-monochromated Mo $K\alpha$ radiation (λ= 0.071 073 nm). The structure of complexes **2** and **3** are solved by direct methods, and the non-hydrogen atoms are located from the trial structure and then refined anisotropically with SHELXTL using a full-matrix least-squares procedure based on F^2 values[23]. The hydrogen atoms positions are fixed geometrically at calculated distances and allowed to ride on the parent atoms. The crystallographic data are summarized in Table 1, while the selected bond lengths and angles are given in Table 2.

CCDC: 689221, **2**; 689222, **3**.

Table 1　Crystal data and structure refinement for complexes 2 and 3

	2	**3**
Formula	$C_{48}H_{68}N_2O_3SiYb$	$C_{88}H_{120}K_2N_4O_4Si_2Yb$
Formula weight	922.20	1 605.30
Crystal system	Monoclinic	Triclinic
Space group	$P2_1$	$P\bar{1}$
a / nm	1.117 39(6)	1.206 7(4)
b / nm	1.977 91(11)	1.363 7(4)
c / nm	2.038 77(11)	1.542 7(5)
α / (°)	90	65.030(5)
β / (°)	97.103 0(10)	68.400(6)
γ / (°)	90	75.468(6)
V / nm^3	4.471 3	2.126 0
Z	4	1
D_c / (g·cm^{-3})	1.370	1.254
μ / mm^{-1}	2.160	1.275
F(000)	1 912	844
Crystal size / mm	0.40×0.35×0.33	0.50×0.40×0.20
Temperature / K	273(2)	293(2)
Tot., uniq. data	32 014, 18 001	15 002, 10 407
R_{int}	0.029 8	0.020 7
Flack parameter	0.009 3	—
Observed data (I>2σ(I))	1 007	457
θ range / (°)	1.01~27.00	1.66~28.35
R_1, wR_2 (all data)	0.040 2, 0.084 7	0.040 3, 0.098 5
S (all data)	0.049 6, 0.089 2	0.055 5, 0.107 7
$(\Delta\rho)_{min}$, $(\Delta\rho)_{max}$ / (e·nm^{-3})	785, 2 945	−353, 650

Table 2 Selected bond lengths (nm) and angles (°) for the complexes 2 and 3

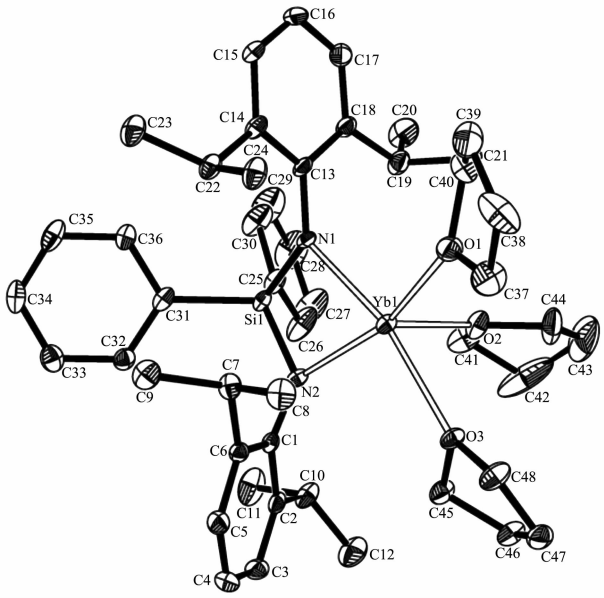
2					
Yb(1)-N(1)	0.234 6(4)	Yb(1)-O(1)	0.245 5(4)	Yb(1)-O(3)	0.249 5(3)
Yb(1)-N(2)	0.239 4(4)	Yb(1)-O(2)	0.237 0(4)		
N(1)-Yb(1)-O(2)	103.58(13)	N(2)-Yb(1)-O(1)	161.64(14)	O(2)-Yb(1)-O(1)	98.85(15)
N(1)-Yb(1)-N(2)	68.80(14)	N(2)-Yb(1)-O(3)	97.94(13)	O(2)-Yb(1)-O(3)	80.59(13)
N(1)-Yb(1)-O(1)	100.16(14)	O(1)-Yb(1)-O(3)	91.84(13)		
N(1)-Yb(1)-O(3)	166.42(13)	O(2)-Yb(1)-N(2)	98.05(14)		
3					
Yb(1)-N(1)	0.245 4(2)	K(1)-O(1)	0.275 1(4)	K(1)-O(2)	0.277 8(4)
Yb(1)-N(2)	0.241 6(2)				
N(2)-Yb(1)-N(1)	66.43(7)	N(2)-Yb(1)-Si(1)a	33.23(5)	N(1)-Yb(1)-Si(1)	146.63(5)
N(2)-Yb(1)-N2a	180.000(1)	N(2)a-Yb(1)-Si(1)a	146.77(5)	N(1)a-Yb(1)-Si(1)	33.37(5)
N(2)a-Yb(1)-N(1)	113.57(7)	N(1)-Yb(1)-Si(1)a	33.37(5)		

Symmetry codes: a: $-x$, $-y+1$, $-z+1$

2 Results and discussion

The use of a dry-box and access to single crystal for X-ray diffraction techniques made it possible to safely handle and characterize the complex. Heterometallic complex with sandwich structure $\{Yb(L)_2[K(THF)_2]_2\}$ (**3**) was readily synthesized as green crystals in one step by 0.5 equiv $[K_2(L)(THF)_2]$. $YbI_2(THF)_2$ in THF at room temperature (Scheme 1). Importantly, when an addition of $YbI_2(THF)_2$ was allowed, another new complex $[Yb(L)(THF)_3]$ (**2**) was isolated as a red solid. Alternatively complex **3** can be synthesized from further reaction of **2** with $[K_2(L)(THF)_2]$, indicating that **2** is an intermediate to the formation of **3**. However, we failed to isolate the other lanthanide(Ⅱ) (Sm and Eu) complexes with homoleptic type like complex **2**.

Compound **2** crystallizes in a monoclinic crystal system with space group $P2_1$. X-ray crystallographic analysis revealed that **2** is mononuclear homoleptic complex with ligand ions coordinated ytterbium center. The structure consists of two independent molecules. This structure differs from homoleptic complexes stabilized by related $\{[(R^1)NC(R^2)]_2C(R^3)\}^-$ $(nacnac^-)$[13] and guanidinate $[(ArN)_2CN(C_6H_{11})_2]^-$ $(Giso^-)$[14-15] ligands including unprecedented examples of 4-coordinate. The coordination geometry of complex **2** is five-coordinated, and the Yb metal center is η^2 (N,N)-coordinated by one amido ligand and three THF molecules, forming a distorted square pyramidal geometry, with N(1), N(2), O(1) and O(3) forming the basal plane whilst O(2) occupying the apical position, as shown in Fig.1. The Yb(Ⅱ)-N bond distances fall in the range of 0.234 6(4)~0.239 4(4) nm, and the N-Yb-N′ angles are 68.8(1)° and 69.1(1)°. The Yb(Ⅱ)-O bond distances range from 0.237 0(4) to 0.249 5(4) nm. Lappert and



All hydrogen atoms are omitted for clarity

Fig.1 Molecular structure of **2** with 30% thermal ellipsoids

co-workers have reported several homoleptic β-diketiminato ytterbium (Ⅱ) complexes. The Yb (Ⅱ)-N bond distances in the latter complexes range from 0.238 6(4) to 0.242 3(9) nm[13], which are slightly longer than those observed for complex **2**.

Over the past years, there has been significant interest in low-coordination-number (<6) lanthanide complexes. Here the coordination sphere includes two chelating L ligands, as shown in Fig.2. Two potassium ion is sandwiched between two phenyl rings via cation -π interactions. In addition to the cation-π interactions with two arene rings, each potassium ion is further bound to two THF molecules. The bis(amido) ligands coordinate in a chelating fashion with Yb-N lengths (Yb(1)-N(1) 0.245 4(2) nm, Yb(1)-N(2) 0.241 6(2) nm) notably longer than those observed in related divalent ytterbium amido species such as complex **2** (Yb(1)-N(1) 0.234 6(4); Yb(1)-N(2) 0.239 4(4) nm). The K-C bond distances ranged from 0.303 2(3) to 0.354 5(4) nm and K(1)-O(1) and K(1)-O(2) bond distances are 0.275 1(4), 0.277 8(4) nm, respectively.

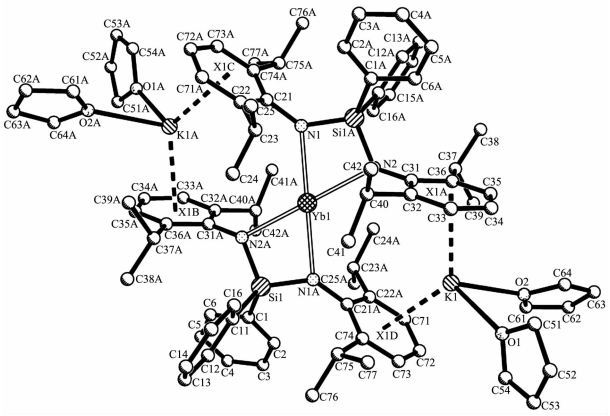


Fig.2　Molecular structure of **3** with all hydrogen atoms omitted for clarity

Over the past several decades, complex $[(C_5Me_5)_2Sm]$ with a sandwich structure has attracted considerable attention in divalent lanthanide chemistry[24-25]. A novel class of triple-decker bent metallocenes complexes of divalent lanthanide $\{(\mu\text{-}\eta^8,\eta^8\text{-cot})[Ln(C_5Me_5)_2]_2\}$ (cot =cyclooctatetraenyl) was reported by Evans[26-27]. The excellent example has a rare tetradecker sandwich complex of a divalent lanthanide $[(C_5Me_5)Yb(\mu\text{-}\eta^8,\eta^8\text{-cot}''')Yb(\mu\text{-}\eta^8,\eta^8\text{-cot}''')Yb(C_5Me_5)]$ (cot'''=1,3,6-tris(trimethylsilyl)cyclo-octatetraenyl-dianion)[28]. Complexes with one, two, or three lanthanide centers can give different types of sandwich structures[23-27]. However, the current type of heterotrimetallic sandwich complex **3** was interesting in lanthanide chemistry.

3　Conclusions

In summary, we have successfully achieved the synthesis of two amido Yb (Ⅱ) complexes **2** and **3**. Complex **2** is an intermediate to the formation of **3**. The structure of complex **3** showed that potassium ions are sandwiched between two phenyl rings and help to stabilize the divalent ytterbium center. We believe that this method should be applicable for the synthesis of complexes of transition metal elements, and this work is in progress in our laboratory and will be reported in due course.

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