

Polymeric ytterbium(II) complex with pyridyl amido ligands

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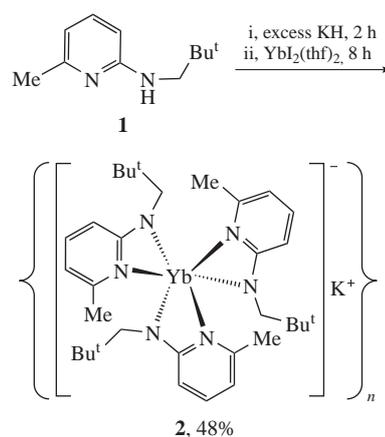
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The reaction of potassium pyridyl amido ligand $\{L = [N(R)(2-C_5H_3N-6-Me)]^-, R = CH_2Bu^t\}$ with $YbI_2(thf)_2$ afforded the linear polymeric complex $[K_{0.5}(L)_3Yb^{II}K_{0.5}]_n$, which was characterized by X-ray structure analysis.

Lanthanide chemistry has been one of the most rapidly developing areas in organometallic chemistry.¹ It is well known that low-valent lanthanides were traditionally restricted to europium, ytterbium and samarium.² The high reducing nature of divalent lanthanide metal centres with their large ionic radii requires that special care must be taken in the choice of the ligands with their proper steric bulk surrounded by the stabilization of lanthanide(II) and reaction conditions to obtain anticipant results.³ Recently, the similar steric ligands of carboranyl, cyclopentadienyl (Cp) and tris(pyrazolyl)borate, which can provide $6e^-$, were found to stabilize lanthanide(II) complexes.⁴ Apart from these ligands, the chemistry of lanthanide(II) amides has received relatively less attention.⁵ In recent years, monoanionic pyridyl amido ligands like $[N(R)(Py)]^-$ with N,N'-chelating fashion have attracted much attention.⁶ Lanthanide(III) complexes supported by the bulky $[N(SiBu^tMe_2)(2-C_5H_3-6-Me)]^-$ ligand have been prepared.⁷ Therefore, the desired synthesis and structural studies of low-valent lanthanide complexes can be performed through careful ligand design. The bulky N,N'-chelating β -diketimines $[\{(R^1)NC(R^2)\}_2C(R^3)]^-$ (nacnac),⁸ guanidinate $[(Ar)_2CN(C_6H_{11})_2]^-$ (Giso)⁹ and unsymmetrical benzamidate $[PhC(NSiMe_3)(NC_6H_3Pr_2-2,6)]^-$ (ref. 10) ligands are known to stabilize Ln^{II} metal centres.

We have synthesised several complexes $[L^{Ph}]_2Ln\{K(sol.)_n\}_2$ ($L^{Ph} = [(RN)_2SiPh_2]^{2-}$, $R = 2,6-Pr_2C_6H_3$, and $Ln = Sm, Yb$ and Eu).^{11–13} These results inspired us to extend the coordination chemistry of bulky pyridyl amido ligands to lanthanide(II) by taking advantage of both the ligand design and cation–nitrogen σ -interactions. Herein, we have used ligand HL ($L = [N(R)(2-C_5H_3N-6-Me)]^-$, $R = CH_2Bu^t$)¹⁴ **1** for the synthesis of the mixed potassium–ytterbium(II) complex $[K_{0.5}(L)_3Yb^{II}K_{0.5}]_n$ **2** with one-dimensional framework (Scheme 1).[†] If we used other R groups such as



Scheme 1

$SiMe_3$ and $SiBu^tMe_2$, a mononuclear ytterbium(II) complex was isolated.¹¹

The use of a dry box and a single crystal X-ray diffraction technique made it possible to safely handle and characterize complex **2** sensitive to air. As shown in Figure 1(a),[‡] each Yb(II) centre exhibits a distorted octahedral geometry surrounded by three N,N'-cheating L ligands. The Yb– N_{amido} bond [2.457 Å (av.)] is shorter than the Yb– $N_{pyridyl}$ bond [2.577 Å (av.)], and the bond distances of K–N ranging from 2.925 to 3.091 Å. In order to further investigate the complexation chemistry of the ligand L towards other divalent lanthanide metals, we carried out the reaction of $SmI_2(thf)_2$ with the potassium salt of pyridyl amide in THF at room temperature and found the deep blue colour of the suspension changing slowly into homogenous bright yellow solution, which

[†] All procedures were performed in a vacuum using standard Schlenk techniques or in a nitrogen-filled dry box. THF was pre-treated with KOH and then distilled from sodium/benzophenone ketyl. Hexane and toluene were purified by distillation from sodium/triglyme benzophenone ketyl or CaH_2 . A solution of HL (0.83 g, 4.6 mmol) in THF (20 ml) was treated with KH (0.2 g, 5 mmol) and TMEDA (0.5 g, 4.3 mmol) under N_2 . A vigorous reaction with effervescence and colour change to yellow was observed in a short time. The reaction mixture was stirred at room temperature for 2 h. The subsequent addition of $YbI_2(thf)_2$ (0.87 g, 1.52 mmol), which was directly prepared by the reaction of excess ytterbium metal with iodine in THF solution for 12 h,¹¹ resulted in an immediate colour change of the reaction mixture to dark purple. After stirring for about 8 h, the solution was filtered and concentrated to ~3 ml. Toluene (4 ml) was added and the resulting mixture was allowed to stand for three days at room temperature. Compound **2** was isolated as large dark red crystals (48% calculated relative to Yb). IR (ν/cm^{-1}): 2963 (s), 2869 (m), 1636 (m), 1608 (w), 1573 (s), 1463 (w), 1447 (m), 1384 (w), 1362 (w), 1252 (s), 1508 (m),

907 (s), 780 (s), 747 (m), 700 (s), 483 (m). Found (%): C, 52.96; H, 6.69; N, 11.14. Calc. for $C_{33}H_{51}KN_6Yb$ (%): C, 53.28; H, 6.91; N, 11.30.

For HL: ¹H NMR (300 MHz, $CDCl_3$) δ : 7.31 (t, 1H, H_{Py}), 6.41 (d, 1H, H_{Py}), 6.19 (d, 1H, H_{Py}), 4.54 (s, 1H, NH), 2.98 (d, 2H, NCH_2), 2.35 (s, 3H, $PyMe$), 0.98 (s, 9H, Bu^t). However, ¹H NMR spectra has been unsuccessfully obtained for Yb^{II} complex **2**. Small amounts of Yb^{III} can have drastic effects on the observed shifts, specific assignment should not be made until data on related complex are obtained.

[‡] Crystal data for **2** ($M = 743.94$, dimensions $0.32 \times 0.25 \times 0.20$ mm). Monoclinic, space group $C2/c$, $a = 12.3648(16)$, $b = 20.285(3)$ and $c = 28.123(4)$ Å, $\beta = 93.548(2)^\circ$, $V = 7040.1$ Å³, $Z = 8$, $d_{calc} = 1.404$ g cm⁻³, $F(000) = 3040$, $\mu(MoK\alpha) = 2.804$ mm⁻¹, $T = 273(2)$ K, $R[I < 2\sigma(I)] = 0.0605$, and the goodness-of-fit on F^2 is 0.994.

CCDC 271910 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2012.

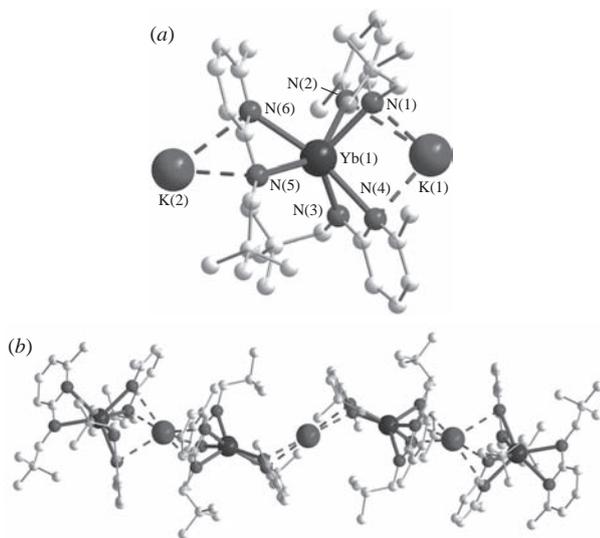


Figure 1 (a) Molecular structure of complex $[KYb^{II}(L)_3]_n$ **2**. (b) Extended structure of **2** showing a one-dimensional network of $[Yb(L)_3]^-$ anions interconnected through K bridging atoms. Selected bond lengths (Å) and bond angles ($^\circ$): Yb(1)–N(1) 2.424(10), Yb(1)–N(2) 2.563(10), Yb(1)–N(3) 2.422(9), Yb(1)–N(4) 2.593(8), Yb(1)–N(5) 2.525(8), Yb(1)–N(6) 2.576(8), K(1)–N(1) 2.925(9), K(1)–N(2) 3.091(11), K(1)–N(3) 3.401(10), K(2)–N(5) 3.069(9), K(2)–N(6) 3.013(9); N(1)–Yb(1)–N(2) 54.3(3), N(3)–Yb(1)–N(4) 53.4(3), N(5)–Yb(1)–N(6) 53.1(3). The K(1) and K(2) have only an occupancy of 0.5 because of its special position, symmetry codes: (i) $1 - x, y, 0.5 - z$; (ii) $1.5 - x, 0.5 - y, -z$.

shows that Sm^{II} was oxidized to Sm^{III} . To the best of our knowledge, the divalent samarium complexes with pyridyl amido ligands have not been reported. Due to stronger reducing power, the failure to prepare Sm^{II} pyridyl amide possibly indicates that pyridyl species may possess an intrinsic instability toward disproportionation, and the corresponding homoleptic complexes were obtained.¹¹

The X-ray structure analysis reveals that the extended structure of **2** [Figure 1(b)], consists of a one-dimensional network of $[Yb(L)_3]^-$ units, with each group anions connected to the other neighbouring units *via* the K^+ bridging atom. This generates a network of $\{-[Yb(L)_3]K[Yb(L)_3]^{-}\}_n$ arrays. The use of lanthanide ions for the construction of coordination polymers and oligomers is more difficult than the use of their *d*-block metal analogues.¹⁵ In the planar four-coordinated Ln^{II} -bis(amido) complexes $[L^{Ph}_2Ln\{K(sol.)_n\}_2]$ ($Ln = Sm, Yb$ and Eu)^{11–13} each potassium ion is sandwiched between two phenyl rings *via* cation–arene π -interactions, which lead to heterometallic complexes. The interaction between alkali metal cations and the π -face of neutral aromatic systems has emerged as an important binding force in a diverse range of biological and chemical settings.¹⁶ The construction of lanthanide–alkali chains,¹⁷ layers¹⁸ and wheels¹⁹ has been a field of rapid growth because of the formation of fascinating structures and their potential applications.²⁰ A linear polymeric structure consisting of samarium(II) atoms surrounded by four π -coordinated pyrrolide rings originating from two ligands, in which the presence of deprotonated N atoms allows additional σ -bonding interactions with alkali metals to occur has been reported.²¹ The structure of complex **2** with a one-dimensional framework is a significant departure from those described in ref. 21, once again emphasizing the remarkable role of the potassium cation in both the structure and metal-to-ligand σ -bonding mode. In organometallic chemistry, attention is focused on the mononuclear complex especially in the low-valent lanthanide chemistry.

In summary, we successfully synthesized and isolated a new polymeric ytterbium(II) complex with the pyridyl amido ligand $[N(R)(2-C_3H_3N-6-Me)]^-$ (L) ($R = CH_2Bu^t$). When R is $SiMe_3$ or $SiBu^tMe_2$, we easily obtained mononuclear $[L']_2Yb^{II}(TMEDA)$ in good yields.¹¹

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