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Introduction

Over the past few decades, there has been a growing interest in the chemistry of organolanthanide complexes supported by various non-cyclopentadienyl ligands.^{1–3} Amido anions $[NR_2]^-$ (R = H, alkyl, aryl or silyl) have proven to be useful ancillary ligands in organolanthanide(II) chemistry.^{3b,4} Amido complexes of Sm(II), Eu(II) and Yb(II) derived from the bulky $[N(SiMe_3)_2]^-$ ligand, and the related $[N(Ph)(SiMe_3)]^-$ and $[NPh_2]^-$ anions have been reported.^{5–7} Besides these three traditional lanthanide(II) ions, it has also been shown that a reaction system containing the $[N(SiMe_3)_2]^-$ ligand and the more reducing Tm(II), Dy(II) or Nd(II) ions has led to a facile reduction of dinitrogen and the isolation of the corresponding $(N_2)^{2-}$ complexes.⁸

2-Pyridyl amides, with a general formula $[N(R)(2-Py)]^-$ (R = H, alkyl, aryl or silyl), are pyridine-functionalized amido ligands which have attracted considerable research interest in the last few decades.⁹ One remarkable property of this class of ligands is their ability to exhibit a flexible coordination

Divalent europium and ytterbium complexes supported by a bulky 2-pyridyl amido ligand: synthesis, structure and reactivity studies†

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Metallation of the *N*-arylated 2-pyridyl amine $[HN(C_6H_3Pr_2^i-2,6)(2-C_5H_3N-6-Me)]$ (1) with potassium hydride in Et₂O and THF yielded potassium amides $[\{KL(OEt_2)\}_2]$ [L = $N(C_6H_3Pr_2^i-2,6)(2-C_5H_3N-6-Me)$] (2) and $KL(THF)_2$ (3), respectively. Treatment of $Lnl_2(THF)_2$ (Ln = Eu, Yb) with 2 afforded the corresponding Ln(II) amido complexes [EuL(μ -L)₂K(THF)] (4) and [YbL₂(THF)₂] (5). In contrast, an analogous reaction of Sml₂(THF)₂ with 2 only led to the isolation of homoleptic Sm(III) triamide [SmL₃] (6). The reaction chemistry of divalent complexes 4 and 5 was examined. Oxidation of the Eu(III) amido complex 4 by iodine yielded the trivalent [EuL₃] (7), whereas addition of Yb(III) diamide 5 to iodine led to the isolation of the bis(amido) Yb(III) iodide complex [YbL₂(I)(THF)] (8). Complex 8 could also be prepared by the reaction of 5 with copper(I) iodide. A subsequent reaction of 8 with KOBu^t gave, unexpectedly, the Yb(III) triamide [YbL₃] (9). Reactions of complex 5 with diphenyl dichalcogenides PhEEPh (E = S, Se, Te) also gave [YbL₃] (9) as the only isolable product. The solid-state structures of complexes 2 and 4–9 were elucidated by X-ray diffraction analysis.

behaviour. They can be bound to metal ions in a monodentate, N,N'-chelating or N,N'-bridging fashion (Chart 1). Additionally, their steric and electronic properties can be readily modified by introduction of various substituents at the amido nitrogen atom or on the pyridyl ring. Accordingly, a number of maingroup, transition-metal and f-element complexes with interesting coordination geometry as well as different degrees of association have been reported.9-20 In recent years, Kempe and co-workers have reported on the synthesis of Sm(II), Eu(II) and Yb(II) complexes supported by several sterically very crowded pyridine-functionalized amido ligands, such as [N(C₆H₃Prⁱ₂-2,6 $\{2-C_5H_3N-6-(C_6H_2Pr_3^i-2,4,6)\}^{-1}$ (Ap*), $[N(C_6H_3Pr_2^i-2,6)-6]$ $\{2-C_5H_3N-6-(C_6H_3Me_2-2,6)\}^{-}$ (Ap'), and $[N(C_6H_2Me_3-2,4,6) \{2-C_5H_3N-6-(C_6H_2Me_3-2,4,6)\}]^-$ (Ap^{Me}).²⁰ It was also reported that a slight modification in the steric bulkiness of these amido ligands could crucially affect the structures of the corresponding lanthanide(II) complexes.



Chart 1 Three common coordination modes of 2-pyridyl amido ligands.

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[†]Electronic supplementary information (ESI) available: Crystallographic information files (CIF), selected bond distances (Å) and angles (°) for complexes **2** and **4–9**, ¹H NMR spectrum of **9**, and ¹H NMR spectra showing the reactions of complex **5** with PhEEPh (E = S and Se). CCDC 866987–866993. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt30333g

We are interested in the coordination chemistry and reactivity of metal complexes supported by anionic nitrogen-based ligands, such as amides^{19,21,22} and amidinates.²³ Earlier, we have studied the coordination behaviour of 2-pyridyl amides with transition-metal^{19a,b} and trivalent lanthanide ions.^{19c} Recently, we have reported on the preparation and reaction chemistry of divalent samarium, europium and ytterbium complexes derived from the bulky amidinate ligand [PhC-(NSiMe₃)(NC₆H₃Prⁱ₂-2,6)]^{-.23b} The 2-pyridyl amide and amidinate systems have one structural similarity: both ligand systems possess an NCN ligand backbone. This leads to the formation of highly strained four-membered MNCN metallacycle rings when these ligands are bonded to the metals in a bidentate manner. In order to compare the coordination properties of these two types of monoanionic N-donor ligands with divalent lanthanide ions, we have prepared a new 2-pyridyl amido ligand, $[N(C_6H_3Pr_2^{i}-2,6)(2-C_5H_3N-6-Me)]^{-}$ (L), which has a steric requirement comparable to that of the amidinate anion [PhC(NSiMe₃)(NC₆H₃Prⁱ₂-2,6)]⁻ recently reported by us.^{23b} Herein, we report on the synthesis and structural characterization of Eu(II) and Yb(II) complexes derived from amido ligand L. The reductive chemistry of these lanthanide(II) amides is also described. To our knowledge, studies on the reducing properties of lanthanide(II) complexes derived from 2-pyridyl amido ligands have been rarely reported in the literature.

Results and discussion

Ligand synthesis

The ligand precursor $[HN(C_6H_3Pr^i_2-2,6)(2-C_5H_3N-6-Me)]$ (1) was prepared by a palladium-catalyzed aryl amination method as developed by Buchwald and co-workers.²⁴ 2,6-

Diisopropylaniline was allowed to react with 2-bromo-6-picoline, in the presence of tris(dibenzylideneacetone)dipalladium(0) $(Pd_2(dba)_3)$ as the catalyst together with 1,3-bis(diphenyl-phosphanyl)propane (DPPP) and NaOBu^t, in toluene at 95 °C for two days. Work-up of the product mixture afforded compound 1 as a pale yellow solid in 80% yield. Subsequent metallation of compound 1 with potassium hydride in diethyl ether and THF solutions vielded potassium amides $[{KL(OEt_2)}_2]$ (2) and $KL(THF)_2$ (3), respectively (Scheme 1). Alternatively, the THFadduct 3 could also be prepared by a transmetallation reaction of lithium amide LiL with KOBu^t in THF. The formulation of complexes 2 and 3 was confirmed by NMR spectroscopy and elemental analysis. The ¹H and ¹³C NMR spectra of both complexes showed one set of resonance signals assignable to ligand L as well as the respective donor solvent molecules (i.e. 1:1 L/Et₂O for 2 and 1:2 L/THF for 3). It is noted that the isopropyl methyl groups of the L ligands on both complexes are diastereotopic and occur as two doublets (at 0.93 and 1.18 ppm for 2, and 1.00 and 1.23 ppm for 3) in their respective ¹H NMR spectra.^{25,26}

The solid-state structure of Et₂O-adduct 2 was determined by single-crystal X-ray diffraction analysis. The molecular structure of complex 2 is illustrated in Fig. 1. Selected bond distances and angles of the complex are provided in Table S1 in ESI.[†] Complex 2 crystallizes in the triclinic space group *P*1. The crystal structure of 2 consists of two potassium ions bridged by a pair of μ – η^2 , η^2 -bound L ligands. The K–N(amido) distances measure 2.772(1) Å [K(1)–N(1)] and 3.006(1) Å [K(1)– N(1)#1], whereas the corresponding K–N(pyridyl) distances are 2.836(2) Å [K(1)–N(2)] and 2.853(2) Å [K(1)–N(2)#1]. The observed K(1)···K(1)#1 distance is 3.346(1) Å. Each potassium ion is further coordinated by one Et₂O solvent molecule, with K(1)–O(1) being 2.704(1) Å.



Scheme 1 Synthesis of complexes 2 and 3.

Synthesis of Eu(II) and Yb(II) amido complexes

Divalent europium and ytterbium complexes of the L ligand were prepared by metathesis reactions of the appropriate lanthanide(II) diiodide with potassium amide $[{KL(OEt_2)}_2]$ (2) (Scheme 2). Treatment of $EuI_2(THF)_2$ with two molar equivalents of 2 in THF at ambient temperature afforded the Eu(II) amido complex $[EuL(\mu-L)_2K(THF)]$ (4), whereas an analogous reaction of YbI₂(THF)₂ with 2 followed by crystallization of the



Fig. 1 Molecular structure of $[\{KL(OEt_2)\}]_2$ (2) (30% thermal ellipsoids) with atom labelling.

product from toluene led to the solvated complex $[YbL_2(THF)_2]$ · 0.25C₇H₈ (5·0.25C₇H₈). Complexes 4 and 5·0.25C₇H₈ were isolated as extremely air-sensitive orange and purple crystals, respectively. The Eu(π) complex is readily soluble in THF and hexane, whereas the Yb(π) complex is soluble in THF and toluene but only sparingly soluble in diethyl ether and hexane. Results of elemental analysis are in good agreement with the formulation of both complexes. The ¹H and ¹³C NMR spectra of the diamagnetic 5·0.25C₇H₈ are consistent with the structure of the complex as shown in Scheme 2. The isopropyl methyl groups of the L ligand are diastereotopic as evidenced by two doublets observed at 1.11 and 1.27 ppm, respectively.

Single crystals of complexes 4 and 5.0.25C₇H₈ suitable for X-ray diffraction were obtained from hexane and toluene, respectively. Both complexes crystallize in the triclinic space group $P\overline{1}$. Fig. 2 shows the molecular structure of complex 4.²⁷ The Eu(II) ion has a six-coordinate ligand environment formed by three L ligands. One of these L ligands is bound to the Eu(II) centre in an N,N'-chelating manner (η^2 -bound), whilst the other two are $\mu - \eta^2$, η^2 -bound to the Eu(II) ion and a potassium ion [K(1)]. The potassium ion is further bonded to one THF molecule. The N,N'-chelating L ligand forms a highly strained, four-membered metallacycle ring with the Eu(II) ion, resulting in an acute N(1)-Eu(1)-N(2) bite angle of 52.1(1)°. The amido nitrogen atom N(1) adopts a nearly trigonal planar geometry (sum of bond angles = 359.1°). The Eu(1)–N(1) bond length of 2.563(3) Å is slightly shorter than the corresponding Eu(II)–N(pyridyl) distance [Eu(1)–N(2)] of 2.605(3) Å. Compared with other Eu(II) amido complexes reported in the literature, the Eu(1)-N(1) bond length in 4 is longer than the terminal Eu(II)-N(amido) distance in the heterobimetallic [Eu{N- $(SiMe_3)_2$ { μ -N $(SiMe_3)_2$ }2Na] [2.448(4) Å],^{5b} and slightly longer



Scheme 2 Synthesis of divalent amido complexes 4 and 5.



Fig. 2 Molecular structure of $[EuL(\mu-L)_2K(THF)]$ (4) (30% thermal ellipsoids) with atom labelling. One of the coordinated THF molecules is 2-fold disordered and only one of the two possible orientations is shown for clarity.

than the corresponding distances reported for the binuclear [{Eu(Ap*)(I)(THF)₂}₂] [2.481(3) Å] and the mononuclear [Eu(Ap*)₂(THF)₂] [2.526(6) and 2.547(6) Å] [Ap* = [N(C₆H₃Prⁱ₂-2,6){2-C₅H₃N-6-(2,4,6-Prⁱ₂C₆H₂)}]⁻].^{20d} The Eu(II)-nitrogen bonds formed by the two μ - η^2 , η^2 -bound L ligands in complex 4 fall within the range of 2.582(3)–2.717(3) Å. They are slightly longer than the bridging Eu(II)–N(amido) distances reported for [Eu{N(SiMe₃)₂}{µ-N(SiMe₃)₂}₂Na] [2.539(4) and 2.554(4) Å].^{5b} The longer Eu(II)–nitrogen bond distances in 4 may be attributed to a sterically more crowded ligand environment generated by L as compared with that of the [N(SiMe₃)₂]⁻ ligand.

The chemistry of a series of heterobimetallic alkali-metallanthanide complexes of the general formula M₃[Ln(binol)₃] (Ln = lanthanide, M = alkali metal, binol = binaphtholates) has been studied in detail by two research groups led independently by Shibasaki²⁸ and Aspinall.²⁹ These complexes were shown to be multifunctional catalysts, which possess a unique combined Lewis acid-BrØnsted base property.28 They can catalyze a wide range of enantioselective transformations. Using a sulfur-bridged binaphtholate ligand (LSN), Arnold and coworkers have reported on the preparation of heterobimetallic tris-ligand complexes of the type $[Li(THF)_3][Ln(L^{SN})_3]$ (Ln = Sm, Eu, Y).³⁰ The latter complexes were prepared by metathesis reactions of the corresponding lanthanide(m) triamide complexes $[Ln{N(SiMe_3)_2}_3]$ with a lithium salt of the L^{SN} ligand, irrespective of ligand-to-metal stoichiometry. Results of these studies on the heterobimetallic alkali-metal-lanthanide binaphtholate complexes can provide us insights on our future reactivity studies involving the heterometallic Eu(II) complex 4.

The solid-state structure of the solvated Yb(π) diamide 5·0.25C₇H₈ is depicted in Fig. 3.²⁷ The Yb(π) centre exhibits a hexacoordinate geometry, with its coordination sphere consisting of two η^2 -bound L ligands and two THF molecules. Each L ligand forms a highly strained, four-membered



Fig. 3 Molecular structure of [YbL₂(THF)₂]-0.25C₇H₈ (**5**·0.25C₇H₈) (30% thermal ellipsoids) with atom labelling. The two coordinated THF molecules are 2-fold disordered and only one of the two possible orientations is shown for clarity. The toluene solvate molecule is also omitted for clarity.

YbNCN metallacycle ring with the Yb(II) ion. The N(1)-Yb(1)-N(2) and N(3)-Yb(1)-N(4) bite angles are acute, namely 55.5(1)° and 54.8(1)°. The amido nitrogen atoms N(1) and N(3) have an almost trigonal planar geometry (sum of bond angles around N(1) and N(3) are 359.8° and 359.4°, respectively). The Yb(II)–N(amido) distances in complex 5 are 2.431(4) Å [Yb(1)– N(1)] and 2.427(4) Å [Yb(1)-N(3)], whereas the corresponding Yb(II)-N(pyridyl) distances are slightly longer, namely 2.453(4) Å [Yb(1)-N(2)] and 2.501(4) Å [Yb(1)-N(4)]. The observed Yb(n)-N(amido) distances in 5 are slightly longer than the terminal Yb(II)-N(amido) bond lengths reported for [Yb{N(SiMe₃)₂}- $\{\mu$ -N(SiMe₃)₂ $\}_2$ Na] [2.38(2) Å]^{5c} and [Yb{NPh(SiMe₃)}_2(THF)]_2 $[2.326(4) \text{ and } 2.353(4) \text{ Å}]^7$ Compared with other Yb(II) complexes supported by sterically hindered pyridine-functionalized amido ligands, the Yb(II)-N(amido) distances in 5 are marginally longer than the corresponding distances reported for the four-coordinate $[Yb(Ap')_2]$ [2.371(1) and 2.404(1) Å],^{20b} the fivecoordinate $[Yb(Ap')_2(THF)]$ [2.380(4) and 2.384(3) Å]^{20b} and the six-coordinate [Yb(Ap^{Me})₂(THF)₂] [2.396(5) Å],^{20b} and similar to those reported for [Yb(Ap*)₂(THF)₂] [2.431(6) and 2.464(7) Å].^{20d}

Attempts to prepare a Sm(II) complex of the L ligand have not been successful. Addition of two molar equivalents of potassium amide 2 to SmI₂(THF)₂ in THF resulted in a dark brown suspension. After work-up, a yellow crystalline product was isolated from the solution (Scheme 3). Both X-ray diffraction data and elemental analysis indicated that the product was the homoleptic Sm(III) triamide [SmL₃] (6). In order to explore other plausible synthetic routes for the desired Sm(II) derivative of L, we also examined the transamination reaction of [Sm{N(SiMe₃)₂}₂(THF)₂] with free 2-pyridyl amine 1. The latter reaction also afforded a brown suspension from which complex 6 was isolated as the only product from the solution.

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Fig. 4 Molecular structure of $[SmL_3]$ (6) (30% thermal ellipsoids) with atom labelling. Only one of the two independent molecules in the asymmetric unit is shown.

Apparently, L may not be a good supporting ligand for the more reducing Sm(n) ion.

The molecular structure of $[SmL_3]$ (6) is depicted in Fig. 4.²⁷ Complex 6 crystallizes in the hexagonal crystal system with space group $P\bar{3}$. The Sm(III) ion is coordinated by three N,N'chelating L ligands, and the complex conforms closely to a C_3 symmetry. The Sm(III)–N(amido) distances [Sm(1)–N(1) 2.363(3) Å and Sm(1)-N(1)#1 2.362(3) Å] are shorter than the distances corresponding Sm(III)–N(pyridyl) [Sm(1)-N(2)]2.503(3) Å]. The amido nitrogen atoms exhibit a trigonal planar geometry (sum of bond angles around $N(1) = 360^{\circ}$). The N(1)-Sm(1)-N(2) bite angle of 55.5(1)° is acute. Earlier, we have reported on the use of the N-silvlated [N(SiBu^tMe₂)(2-C₅H₃N-6-Me)]⁻ ligand in the preparation of homoleptic Ce(m) and Nd(III) triamides.^{19c} The latter complexes were prepared by the reactions of anhydrous $LnCl_3$ (Ln = Ce, Nd) with three molar equivalents of a potassium salt of [N(SiBu^tMe₂)(2-C₅H₃N-6Me)]⁻. The corresponding Sm(m) derivative, [Sm{N(SiBu^tMe₂)-(2-C₅H₃N-6-Me)}₃], was also prepared in our laboratory by using a similar procedure.³¹ The structural parameters of complex **6** are comparable to those observed in the [Sm-{N(SiBu^tMe₂)(2-C₅H₃N-6-Me)}₃] complex.

Reaction chemistry of $[EuL(\mu\text{-}L)_2K(THF)]$ (4) and $[YbL_2(THF)_2]$ (5)

One interesting feature of organolanthanide(π) compounds is their highly reducing reactivity.³² The redox chemistry of lanthanide(π) metallocene complexes has been studied in detail.^{33–36} On the other hand, there were only a few reports on the redox chemistry of lanthanide(π) complexes supported by non-cyclopentadienyl systems.^{37,38} An interesting issue in organolanthanide(π) chemistry is to understand the effects of steric and electronic properties of different ligands on the redox reactivity of lanthanide(π) complexes. Recently, we have reported on the reactions of a few lanthanide(π) amidinate complexes with iodine, diphenyl dichalcogenides PhEEPh (E = Se, Te) and *N*,*N'*-dicyclohexylcarbodiimide.^{23b} In order to compare the redox reactivity of lanthanide(π) complexes supported by amido and amidinato ligands, we have carried out an initial study on the reduction chemistry of complexes **4** and **5** in this work.

1. Reactions of complexes 4 and 5 with iodine. Oxidation of the Eu(II) complex 4 with iodine led to the isolation of purple, crystalline Eu(m) triamide $[EuL_3]$ (7) (Scheme 4). Apparently, the presence of three L ligands in the coordination sphere of the Eu(II) ion in 4 favours the formation of the homoleptic triamide 7, instead of a mixed amide-iodide species "EuL₂(I)". The molecular structure of complex 7 was determined by X-ray crystallography (Fig. 5).²⁷ Complex 7 crystallizes in the hexagonal crystal system with space group P3, and is isostructural to the Sm(m) triamide 6. Each L ligand is bonded to the Eu(π) ion in an N,N'-chelating manner, with an acute N(1)-Eu(1)-N(2) bite angle of 55.68(6)°. The amido nitrogen atom N(1) displays a nearly trigonal planar geometry (sum of bond angles around $N(1) = 360^{\circ}$). The observed Eu(III)-N(amido) distance in 7 is 2.350(1) Å [Eu(1)–N(1)], whereas the corresponding Eu(m)-N(pyridyl) distances are slightly longer [Eu(1)-N(2) 2.492(1) Å]. The europium-nitrogen bond distances in 7 are shorter than the corresponding bond lengths observed in the Eu(II) amido complex 4. These differences may



Scheme 4



Fig. 5 Molecular structure of $[EuL_3]$ (7) (30% thermal ellipsoids) with atom labelling. Only one of the two independent molecules in the asymmetric unit is shown.

be attributed to a smaller ionic radius of $Eu(\ensuremath{\mathrm{III}})$ as compared to that of $Eu(\ensuremath{\mathrm{II}}).$

Treatment of Yb(II) diamide 5 with iodine afforded the mononuclear Yb(III) complex [YbL₂(I)(THF)] (8) in 45% yield (Scheme 5). Alternatively, complex 8 could also be prepared by the reaction of 5 with copper(I) iodide in 60% isolated yield. Fig. 6 shows the X-ray structure of complex 8.²⁷ The Yb(III) centre is coordinated by two η^2 -bound L ligands, one iodide ligand and one THF molecule. The coordination geometry around the Yb(III) ion can be described as distorted octahedral. The Yb(III)–N(a) 2.265(2) Å] in 8 are shorter than the corresponding Yb(III)–N(pyridyI) distances [Yb(1)–N(2) 2.363(3) Å and Yb(1)–N(4) 2.366(2) Å]. The bite angles subtended by each of the two L ligands, 58.50(9)° [N(1)–Yb(1)–N(2)] and 58.42(8)° [N(3)–Yb(1)–N(4)], are acute. The Yb(1)–I(1) and Yb(1)–O(1) distances are 2.9205(3) Å and 2.362(2) Å, respectively.

2. Treatment of $[YbL_2(I)(THF)]$ (8) with KOBu^t. It is noted that the presence of an iodide ligand in complex 8 may allow further metathesis reactions of the complex with other anionic ligands. Accordingly, we attempted to prepare a mixed-ligand Yb(m) diamide-alkoxide complex by treatment of 8 with KOBu^t. Addition of 8 to a slurry of KOBu^t in THF resulted in a yellow suspension from which the homoleptic Yb(m) triamide [YbL₃] (9) was isolated as the only product in our hands (Scheme 6). Elemental analysis and NMR spectroscopic data agree with the formulation of complex 9. The ¹H NMR spectrum of 9 showed one set of isotropically shifted signals, which were assignable to the L ligand. The solid-state structure of complex 9 was elucidated by single-crystal X-ray crystallography (Fig. 7).²⁷ Complex 9 crystallizes in the triclinic crystal system with space group $P\bar{3}$, and is isostructural to the Sm(III) and Eu(III) counterparts 6 and 7. The Yb(III) centre in 9 is six-coordinated by three η^2 -bound L ligands. The N(1)-Yb(1)-N(2) bite angle of 58.1° is acute. The amido nitrogen atoms in 9 also adopt a trigonal planar geometry (sum of bond angles around $N(1) = 360^{\circ}$). The Yb(m)-N(amido) distance of 2.270(6) Å [Yb(1)-N(1)] is somewhat shorter than the corresponding Yb(III)-N(pyridyl) distance of 2.388(5) [Yb(1)–N(2)]. Compared to other homoleptic Yb(III) triamide complexes derived from pyridine-functionalized amido ligands, the Yb(1)-N(1) distance in 9 is close to the corresponding distances reported for $[Yb(Ap^{Me})_3]^{20b}$ [2.263(7)-2.299(7) Å] and $[Yb{N(SiBu^tMe_2)(2-C_5H_3N-6-Me)}_3]$ [2.257(4)-2.300(4) Å].³¹ The Yb(1)-N(2) bond length in our current complex is also comparable to the Yb(III)-N(pyridyl) distances observed in [Yb(Ap^{Me})₃]^{20b} [2.357(8)-2.543(7) Å] and $[Yb{N(SiBu^{t}Me_{2})(2-C_{5}H_{3}N-6-Me)}_{3}][2.349(4)-2.375(4) Å]^{.31}$

The factors that give rise to the ligand redistribution and the formation of the Yb(m) triamide **9** remain unclear to us at this stage of our study. One plausible reason may be attributed to the steric bulkiness of the alkoxide ligand. Accordingly, complex [YbL₂(1)(THF)] (**8**) was allowed to react with the sterically less demanding NaOMe under similar reaction conditions.³⁹ Unfortunately, only an intractable oil was obtained after the reaction. The crude product mixture was characterised by ¹H NMR spectroscopy, which revealed the presence of complex [YbL₃] (**9**) as the major product in the mixture together with some unidentified paramagnetic species. Apparently, the size of the alkoxide ligands did not play a key role in the ligand redistribution reaction.

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 $\label{eq:scheme 5} \textbf{Scheme 5} \quad \text{Reactions of complex 5 with } I_2 \text{ and Cul.}$



Fig. 6 Molecular structure of [YbL₂(I)(THF)] **(8)** (30% thermal ellipsoids) with atom labelling. The coordinated THF molecule is 2-fold disordered and only one of the two possible orientations is shown for clarity.

3. Reactions of complex 5 with PhEEPh (E = S, Se, Te). Besides iodine, we have also examined the redox chemistry of Yb(II) diamide 5 with diphenyl dichalcogenides PhEEPh (E = S, Se, Te). Addition of PhEEPh to a solution of 5 in THF afforded a yellow solution from which the homoleptic [YbL₃] (9) was isolated as the only product, though the product yields were modest (Scheme 7). Recently, we have reported on the reactions of Ln(II) (Ln = Sm, Eu, Yb) bis(amidinate) complexes with PhEEPh (E = Se, Te), which yielded the respective Ln(III) amidinate-chalcogenolate complexes. Unfortunately, the expected Yb(III) bisamide-chalcogenolate complexes have not been isolated in this work.⁴⁰

Summary

The coordination properties of the bulky, monoanionic 2-pyridyl amido ligand $[N(C_6H_3Pr^i_2-2,6)(2-C_5H_3N-6-Me)]^-$ (L)

towards Eu(II), Yb(II) and Sm(II) ions were studied in this work. Divalent amido complexes $[EuL(\mu-L)_2K(THF)]$ (4) and $[YbL_2(THF)_2]$ (5) were successfully prepared by the reactions of the appropriate $LnI_2(THF)_2$ (Ln = Eu, Yb) with potassium amide $[{KL(OEt_2)}_2]$ (2). The difference in the structures of 4 and 5 (i.e. an ate-complex versus a neutral mononuclear complex) may be attributed to the different ionic size of Eu²⁺ (0.947 Å) and Yb³⁺ (0.868 Å).⁴¹ Unfortunately, attempts to prepare a Sm(n) complex of L have been unsuccessful. In our hands, only the homoleptic Sm(III) triamide $[SmL_3]$ (6) was isolated. An initial study on the reduction chemistry of complexes 4 and 5 was also carried out in this work. Complexes 4 and 5 reacted readily with iodine to yield trivalent complexes [EuL₃] (7) and [YbL₂(I)(THF)] (8), respectively. Unexpectedly, addition of 5 to diphenyl dichalcogenides, and a further reaction of 8 with KOBu^t gave the homoleptic [YbL₃] (9) as the only isolable product. These results were contrasted to those we obtained earlier with divalent lanthanide complexes of the amidinate anion [PhC(NSiMe₃)(NC₆H₃Prⁱ₂-2,6)]⁻.^{23b} Although both ligand L and the latter amidinate are monoanionic bridging ligands with similar steric properties, they showed different coordination behaviour towards divalent lanthanide ions, particularly the Sm(II) ion. Additionally, based on the results of our initial reactivity studies, the 2-pyridyl amido ligand L may have a higher tendency to form homoleptic lanthanide(III) triamides, probably due to its intrinsic steric and electronic properties.

Experimental

General procedures

All manipulations were carried out using standard Schlenk techniques or in a Braun MB 150-M dry box under an atmosphere of purified nitrogen. Solvents were dried over a sodium wire and distilled under nitrogen from sodium benzophenone (diethyl ether and THF), Na/K alloy (toluene) or calcium hydride (hexane), and degassed twice by freeze–thaw cycles before use. 2,6-Diisopropylaniline was distilled over KOH before use. All other reagents were used as received. $LnI_2(THF)_2 (Ln = Sm, Eu, Yb)^{42-44}$ and $[Sm{N(SiMe_3)_2}_2(THF)_2]^6$ were prepared according to literature procedures. ¹H and ¹³C NMR spectra were recorded on a Bruker DPX300 NMR

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Scheme 6 Reaction of complex **8** with KOBu^t.



Fig. 7 Molecular structure of $[YbL_3]\ (9)\ (30\%$ thermal ellipsoids) with atom labelling.

spectrometer (at 300.13 and 75.47 MHz) or a Bruker Advance III 400 NMR spectrometer (at 400.13 and 100.61 MHz). Chemical shifts were referenced to residue protons of CDCl₃ and C_6D_6 at 7.26 and 7.16 ppm (in ¹H NMR), and 77.16 and 128.06 ppm (in ¹³C NMR), respectively. Melting-points were recorded on an Electrothermal melting-point apparatus and were uncorrected. Mass spectra were obtained on a Thermo-Finnigan MAT 95 XP Mass Spectrometer (E.I. 70 eV). Elemental analyses (C, H, N) were performed by MEDAC Ltd., Brunel University, U.K.

Synthesis of $[HN(C_6H_3Pr_2^i-2,6)(2-C_5H_3N-6-Me)]$ (HL) (1). To a mixture of sodium *tert*-butoxide (2.56 g, 26.64 mmol), tris-(dibenzylideneacetone)dipalladium(0) (0.25 g, 0.27 mmol) and 1,3-bis(diphenylphosphanyl)propane (0.34 g, 0.81 mmol) in toluene (20 cm³) was added a solution of 2,6-Pr₂ⁱ₂C₆H₃NH₂ (4.78 g, 27.0 mmol) and 2-BrC₅H₃N-6-Me (4.53 g, 26.3 mmol) in the same solvent (20 cm³). The reaction mixture was stirred at 95 °C for 3 days, and then quenched with water (10 cm³). The resulting mixture was extracted with diethyl ether (2 × 30 cm³). The combined organic layer was washed with saturated sodium chloride solution and dried over magnesium sulphate. All the volatiles were then removed under reduced pressure to give a brown solid. The crude product was purified by column chromatography (CH₂Cl₂) to give compound **1** as a pale yellow solid. Yield: 5.64 g, 21.1 mmol (80%). ¹H NMR (300.13 MHz, CDCl₃): δ 7.32 (dd, J = 6.6, 8.6 Hz, 1H, p-ArH), 7.26–7.20 (m, 3H, *m*-ArH and PyH), 6.48 (d, J = 7.3 Hz, 1H, PyH), 6.05 (br, 1H, NH), 5.74 (d, J = 8.3 Hz, 1H, PyH), 3.21 (sept, J = 6.9 Hz, 2H, CHMe₂), 2.43 (s, 3H, PyMe), 1.13 (d, J = 6.9 Hz, 12H, CHMe₂). ¹³C NMR (75.47 MHz, CDCl₃): δ 159.0, 157.2, 148.1, 138.2, 133.7, 128.1, 124.1, 112.9, 102.6, 28.4, 24.4, 24.0. MS (E.I. 70 eV): m/z (%) [M]⁺ 268 (17), [M - CH₃]⁺ 253 (11), [M - Prⁱ]⁺ 225 (100). HRMS (LSI): m/z calc. for C₁₈H₂₄N₂ [M + H]⁺ 268.1934, found: 268.1940.

Synthesis of $[{KL(OEt_2)}_2]$ (2). A solution of compound 1 (5.48 g, 20.5 mmol) in diethyl ether (15 cm³) was added to a slurry of KH (0.99 g, 24.8 mmol) in the same solvent (10 cm³) at 0 °C. The reaction mixture was stirred at room temperature for 1 day, filtered, and the filtrate was concentrated in vacuo to ca. 10 cm³. The *title* compound was obtained as colourless crystals at room temperature. Yield: 6.21 g, 16.3 mmol (80%). M.p. = 261–266 °C. ¹H NMR (400.13 MHz, C_6D_6): δ 7.22–7.11 (m, 6H, ArH), 6.93 (dd, J = 6.7, 8.6 Hz, 2H, PyH), 5.93 (d, J = 6.7 Hz, 2H, PyH), 5.64 (d, J = 8.6 Hz, 2H, PyH), 3.25 (q, J = 7.0 Hz, 8H, OCH₂CH₃), 2.92 (sept, J = 6.9 Hz, 4H, CHMe₂), 2.25 (s, 6H, PyMe), 1.18 (br, 12H, CHMe₂), 1.11 (t, J = 7.0 Hz, 12H, OCH₂CH₃), 0.93 (br, 12H, CHMe₂). ¹³C NMR (100.61 MHz, C_6D_6): δ 166.8, 155.8, 150.1, 141.7, 137.3, 123.8, 121.4, 105.4, 102.8, 65.9, 28.1, 25.9, 24.1, 15.5. Anal. calc. for C44H66K2N4O2: C, 69.43; H, 8.74; N, 7.36%. Found: C, 69.02; H, 8.97; N, 7.88%.

Synthesis of KL(THF)₂ (3). Method A: Compound 3 was prepared by a procedure similar to that of 2 described above, except that THF was used as the solvent. Reagents used: [HL] (1), 3.77 g, 14.1 mmol; KH, 0.64 g, 16.0 mmol. The product was obtained as a colourless crystalline solid. Yield: 4.62 g, 10.3 mmol (73%). M.p.: 261–266 °C. ¹H NMR (400.13 MHz, C₆D₆): δ 7.25 (d, *J* = 7.6 Hz, 2H, *m*-ArH), 7.14 (m, 1H, *p*-ArH), 6.92 (dd, *J* = 6.7, 8.6 Hz, 1H, PyH), 5.88(d, *J* = 6.7 Hz, 1H, PyH), 5.67 (d, *J* = 8.6 Hz, 1H, PyH), 3.48 (m, 8H, THF), 3.03 (sept, *J* = 6.9 Hz, 2H, *CH*Me₂), 2.21 (s, 3H, PyMe), 1.38 (m, 8H, THF),



1.23 (br, 6H, CHMe₂), 1.00 (br, 6H, CHMe₂). ¹³C NMR (100.62 MHz, C₆D₆): δ 166.8, 156.0, 150.3, 141.8, 137.3, 123.8, 121.4, 105.4, 102.7, 67.8, 28.2, 25.8, 25.7, 24.3, 24.1. Anal. calc. for C₂₆H₃₉KN₂O₂: C, 69.29; H, 8.72; N, 6.21%. Found: C, 69.03; H, 8.64; N, 6.55%.

Method B: A solution of LiBu^{*n*} (1.6 M in hexanes, 8.93 cm³, 14.3 mmol) was added to a solution of compound **1** (3.80 g, 14.2 mmol) in THF (15 cm³) at 0 °C. The reaction mixture was stirred at room temperature for 4 h and then added directly to a slurry of KOBu^{*t*} (1.59 g, 14.2 mmol) in THF (10 cm³) at 0 °C. The resultant mixture was stirred at room temperature for another period of 12 h. All the volatiles were then removed *in vacuo* to give a yellow solid. It was washed with hexane (30 cm³) and re-dissolved in THF (30 cm³). After filtration, the solution was concentrated under reduced pressure to *ca.* 10 cm³. Standing the solution at room temperature for 1 day gave complex **3** as colourless crystals. Yield: 3.96 g, 8.81 mmol (62%).

Synthesis of $[EuL(\mu-L)_2K(THF)]$ (4). A solution of $[{KL-(OEt_2)}_2]$ (2) (1.67 g, 4.38 mmol) in THF (15 cm³) was added to a solution of $EuI_2(THF)_2$ (1.21 g, 2.20 mmol) in the same solvent (15 cm³). The reaction mixture was stirred at room temperature for 1 day to give an orange-red suspension. The solution was pumped to dryness and the residue was extracted with hexane. The hexane extract was concentrated under reduced pressure to give complex 4 as orange crystals. Yield: 0.90 g, 0.85 mmol (39%). M.p.: 190–193 °C. Anal. calc. for C₅₈H₇₇EuKN₆O: C, 65.39; H, 7.28; N, 7.88%. Found: C, 64.79; H, 7.98; N, 8.45%.

Synthesis of $[YbL_2(THF)_2] \cdot 0.25C_7H_8$ (5 $\cdot 0.25C_7H_8$). To a solution of $YbI_2(THF)_2$ (2.21 g, 3.86 mmol) in THF (15 cm³) was added a solution of $[\{KL(OEt_2)\}_2]$ (2) (2.30 g, 3.02 mmol) in the same solvent (15 cm³) at room temperature. The reaction mixture was stirred at room temperature for 1 day. All the volatiles were removed under reduced pressure to give a dark purple solid residue. The residue was extracted with toluene and filtered. Concentration of the resulting solution yielded the title compound as deep purple block-shaped crystals. Yield: 1.98 g, 2.33 mmol (77%). M.p.: 216–219 °C. ¹H NMR (400.13 MHz, C₆D₆): δ 7.28 (d, J = 7.5 Hz, 4H, *m*-ArH), 7.21–7.12 (m, 1.25H, *Ph*Me), 7.03 (t, J = 7.5 Hz, 2H, *P*-ArH), 6.89 (dd, J = 6.9, 8.6 Hz, 2H, PyH), 5.86 (d, J = 6.9 Hz, 2H, PyH), 5.66 (d, J = 8.6 Hz, 2H, PyH), 3.49 (br, 12H, THF and CHMe₂), 2.18

(s, 6H, Py*Me*), 2.11 (s, 0.75H, Ph*Me*), 1.27 (d, J = 6.8 Hz, 12H, CH*Me*₂), 1.22 (br, 8H, THF), 1.11 (d, J = 6.8 Hz, 12H, CH*Me*₂). ¹³C NMR (100.62 MHz, C₆D₆): δ 168.7, 153.8, 147.9, 143.5, 138.0, 123.6, 122.8, 105.2, 104.1, 68.7, 28.1, 25.4, 25.2, 24.3, 23.9, 21.4. Anal. calc. for C₄₄H₆₂N₄O₂Yb·C₇H₈: C, 64.88; H, 7.47; N, 5.93%. Found: C, 64.42; H, 7.61; N, 6.19%.

Reaction of SmI₂(THF)₂ with [{KL(Et₂O)}₂] (2). A solution of $[{KL(Et_2O)}_2]$ (2) (1.95 g, 5.12 mmol) in THF (15 cm³) was slowly added to a solution of SmI₂(THF)₂ (1.56 g, 2.84 mmol) in the same solvent (15 cm³). The reaction mixture was stirred at room temperature for 1 day, whereupon its colour changed gradually from dark blue to dark brown. The solution was pumped to dryness and the residue was extracted with hexane. Concentration of the solution yielded complex $[SmL_3]$ (6) as yellow crystals. Yield: 0.72 g, 0.76 mmol (30%). M.p.: decomposed at 357-359 °C without melting. ¹H NMR (400.13 MHz, C_6D_6): δ 12.55 (br, 3H, CHMe₂), 9.02 (d, J = 8.6 Hz, 3H, PyH), 8.19 (dd, J = 7.2, 8.6 Hz, 3H, PyH), 8.04 (dd, J = 1.3, 7.7 Hz, 3H, *m*-Ar*H*), 7.18–7.14 (m, 3H, *p*-Ar*H*), 5.59 (dd, *J* = 1.3, 7.7 Hz, 3H, *m*-Ar*H*), 5.47 (d, *J* = 7.2 Hz, 3H, Py*H*), 3.86 (d, *J* = 6.5 Hz, 9H, $CHMe_2$), 3.11 (d, J = 6.5 Hz, 9H, $CHMe_2$), 1.16 (d, J = 6.3 Hz, 9H, CHMe2), 0.7 (br, 3H, CHMe2), -3.9 (s, 9H, PyMe), -6.5 (d, J = 6.3 Hz, 9H CHMe₂). ¹³C NMR (100.62 MHz, C₆D₆): δ 151.0, 146.9, 144.9, 141.8, 140.5, 125.6, 123.5, 111.3, 104.5, 34.5, 27.8, 27.1, 26.3, 24.0, 19.3, 17.0. Anal. calc. for C54H69N6Sm: C, 68.09; H, 7.30; N, 8.82%. Found: C, 67.55; H, 7.36; N, 9.59%.

Reaction of $[Sm{N(SiMe_3)_2}_2(THF)_2]$ with $[HN(C_6H_3Pr_2^i-2.6)-(2-C_5H_3N-6-Me)]$ (1). Compound 1 (1.34 g, 5.03 mmol) was added to a purple solution of $[Sm{N(SiMe_3)_2}_2(THF)_2]$ (1.54 g, 2.51 mmol) in hexane (30 cm³) at 0 °C. The reaction mixture was stirred at room temperature for 8 h, whereupon a dark brown suspension was obtained. The brown suspension was filtered and the filtrate was evaporated to dryness under reduced pressure. The resulting dark brown residue was extracted with toluene. Concentration of the solution under reduced pressure yielded complex 6 as a yellow crystalline solid. Yield: 0.44 g, 0.46 mmol (18%).

Reaction of $[EuL(\mu-L)_2K(THF)]$ (4) with I₂. To a solution of complex 4 (1.96 g, 1.84 mmol) in THF (20 cm³) at 0 °C was slowly added a solution of I₂ (0.23 g, 0.89 mmol) in THF (10 cm³). The reaction mixture was stirred at room temperature for 1 day. All the volatiles were removed *in vacuo* and the solid

residue was extracted with hexane. Concentration of the solution gave complex $[EuL_3]$ (7) as purple crystals. Yield: 1.12 g, 1.17 mmol (64%). M.p.: 378–380 °C (dec.). Anal. calc. for $C_{54}H_{69}EuN_6$: C, 67.98; H, 7.29; N, 8.80%. Found: C, 67.55; H, 7.58; N, 8.92%.

Reaction of [YbL₂(THF)₂] (5) with I₂. To a solution of complex 5 (1.64 g, 1.92 mmol) in THF (20 cm³) at 0 °C was slowly added a solution of I₂ (0.25 g, 0.97 mmol) in the same solvent (10 cm³). The reaction mixture was allowed to warm to room temperature and stirring was continued for 1 day, after which the solution was filtered and concentrated under reduced pressure to give [YbL₂(1)(THF)] (8) as orange-red crystals. Yield: 0.78 g, 0.86 mmol (45%). M.p.: 241–243 °C (dec.). Anal. calc. for $C_{40}H_{54}N_4OIYb$: C, 52.98; H, 6.00; N, 6.18%. Found: C, 52.69; H, 6.15; N, 6.29%.

Table 1 Selected crystallographic data^a for complexes **2 4–6** and **7–9**

Reaction of [YbL₂(THF)₂] (5) with CuI. A solution of complex 5 (1.41 g, 1.65 mmol) in THF (20 cm³) was slowly added to a slurry of CuI (0.32 g, 1.7 mmol) in the same solvent (10 cm³). The reaction mixture was stirred at room temperature for 1 day, whereupon its colour changed from dark purple to orange-red. The resulting solution was filtered and concentrated under reduced pressure to give [YbL₂(I)(THF)] (8) as orange-red crystals. Yield: 0.83 g, 0.92 mmol (56%).

Reaction of [YbL₂(I)(THF)] (8) with KOBu^{*t*}. A solution of [YbL₂(I)(THF)] (8) (0.12 g, 1.1 mmol) in THF (20 cm³) at 0 °C was slowly added to a slurry of KOBu^{*t*} (0.83 g, 0.92 mmol) in THF (10 cm³). The resulting mixture was stirred at room temperature for 1 day, after which all the volatiles were removed *in vacuo*. The solid residue obtained was extracted with toluene. Filtration followed by concentration of the solution

	2	4	$5 \cdot 0.25 C_7 H_8$	6
Molecular formula	$C_{44}H_{66}K_2N_4O_2$	C58H77EuKN6O	C44H62N4O2Yb.0.25C7H8	C54H69N6Sm
Molecular weight	761.20	1065.32	875.05	952.50
Crystal size (mm ³)	$0.50 \times 0.40 \times 0.30$	$0.50 \times 0.40 \times 0.30$	$0.40 \times 0.30 \times 0.20$	$0.40 \times 0.30 \times 0.20$
Crystal system	Triclinic	Triclinic	Triclinic	Hexagonal
Space group	PĪ	PĪ	PĪ	P3
$a(\mathbf{\hat{A}})$	10 2513(9)	11 870(2)	10 4629(17)	12673(2)
$h(\Lambda)$	11.020(0)	12542(2)	12.0070(10)	12.073(2) 12.672(2)
$D(\mathbf{A})$	11.0030(9)	13.342(2)	20, 902(2)	12.075(2)
$\mathcal{L}(\mathbf{A})$	(2, 1070(10))	22.292(4)	20.892(3)	18.424(3)
α (°)	62.18/0(10)	98.072(3)	92.854(3)	90
β (0)	89.257(2)	99.164(3)	90.430(3)	90
γ (°)	77.994(2)	112.940(3)	110.628(2)	120
Z	1	2	2	2
$V(A^3)$	1141.54(17)	3175.8(9)	2452.6(7)	2562.7(8)
Density (g cm $^{-3}$)	1.107	1.114	1.185	1.234
Abs coeff. (mm^{-1})	0.244	1.090	1.942	1.185
Temperature (K)	173(2)	293(2)	293(2)	293(2)
Reflections collected	12 915	17 254	13 360	14 233
Independent reflections	$4021 (R_{int} = 0.0774)$	$11114(R_{int}=0.0354)$	$8588 (R_{int} = 0.0340)$	$3112 (R_{int} = 0.0520)$
Obs. data with $L > 2\sigma(I)$	3107	8868	7243	2677
Final <i>R</i> indices $[I > 2\sigma(I)]^b$	$R_{\rm c} = 0.0520 \ \text{w}R_{\rm c} = 0.1368$	$R_{\rm c} = 0.0434 \text{ w}R_{\rm c} = 0.0990$	$P_{-} = 0.0448 \text{ w} P_{-} = 0.1180$	$P_{\rm c} = 0.0336 \text{ w} P_{\rm c} = 0.0846$
$P_{\text{indices}} (all data)^{b}$	$R_1 = 0.0520, wR_2 = 0.1500$	$R_1 = 0.0434, WR_2 = 0.0990$	$R_1 = 0.0440, WR_2 = 0.1100$	$R_1 = 0.0350, WR_2 = 0.0040$
	$K_1 = 0.0722$, $WK_2 = 0.1317$	$K_1 = 0.0382, WK_2 = 0.1031$	$K_1 = 0.0334, WK_2 = 0.1240$	$K_1 = 0.0431, WK_2 = 0.1023$
	7	8		9
Molecular formula	C54H69EuN6	$C_{40}H_{5}$	4IN4OAp	C54H69N6Yb
Molecular weight	954.11	906.81		975.19
Crystal size (mm ³)	$0.40 \times 0.30 \times 0.30$	0.40 imes	0.30×0.20	$0.50 \times 0.40 \times 0.30$
Crystal system	Hexagonal	Mono	elinie	Hexagonal
Space group	PĪ	$P2_{1}/c$		P3
a(A)	12.6538(8)	19.242	(5)	12.576(2)
$h(\mathbf{A})$	12,6538(8)	12.623	57(3)	12.576(2)
$c(\dot{A})$	18 4222(12)	17 842	25(4)	18 465(3)
α (°)	90	90		90
$\beta(0)$	90	100.40	90(10)	90
p()	120	100.40	80(10)	120
γ(°)	120	90		120
\mathcal{L}	2	4		2
$V(\mathbf{A}^{\circ})$	2554.5(3)	4262.7	5(18)	2529.1(8)
Density (g cm ⁻³)	1.240	1.413		1.281
Abs coeff. (mm ⁻¹)	1.267	2.950		1.889
Temperature (K)	293(2)	296(2)		296(2)
Reflections collected	21 005	39 618		22 027
Independent reflections	$3103 (R_{int} = 0.0412)$	2) 7711 ($R_{\rm int} = 0.0376)$	$3059 (R_{int} = 0.0701)$
Obs. data with $I \ge 2\sigma(I)$	2783	6816		2699
Final R indices $[I \ge 2\sigma(I)]^b$	$R_1 = 0.0221, WR_2 =$	0.0569 $R_1 = 0.0569$	$0.0253, WR_2 = 0.0629$	$R_1 = 0.0584, WR_2 = 0.1525$
R indices (all data) ^b	$R_1 = 0.0275, WR_2 =$	0.0591 $R_1 = 0.0591$	$0300, wR_2 = 0.0647$	$R_1 = 0.0670, WR_2 = 0.1577$

^{*a*} Data collected on a Bruker SMART CCD diffractometer or a Bruker KAPPA APEX II diffractometer with graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) using ω scan. ^{*b*} $R_1 = \sum ||F_0| - |F_c|| / \sum |F_0|$; w $R_2 = \{\sum [w(F_0^{-2} - F_c^{-2})^2] / \sum [w(F_0^{-2} -$

gave [YbL₃] (9) as yellow crystals. Yield: 0.20 g, 0.20 mmol (22%). M.p.: 219–220 °C (dec.). ¹H NMR (400.13 MHz, C_6D_6): δ 67.00 (s, 9H, *Me*), 61.84 (s, 9H, *Me*), 43.49 (br, 3H, CHMe₂), 19.07 (s, 3H, ArH or PyH), 8.60 (s, 3H, ArH or PyH), 6.60 (s, 3H, ArH or PyH), -1.27 (s, 9H, *Me*), -2.85 (s, 3H, ArH or PyH), -8.76 (s, 3H, ArH or PyH), -20.11 (s, 9H, *Me*), -34.19 (s, 3H, ArH or PyH), -98.47 (br, 3H, CHMe₂). Anal. calc. for $C_{54}H_{69}N_6$ Yb: C, 66.51; H, 7.31; N, 8.61%. Found: C, 65.81; H, 7.59; N, 8.93%.

Reaction of [YbL₂(THF)₂] (5) with PhSSPh. To a solution of PhSSPh (0.12 g, 0.54 mmol) in THF (10 cm³) at 0 °C was added dropwise a solution of $[YbL_2(THF)_2]$ (5) (0.87 g, 1.0 mmol) in the same solvent (20 cm³). After stirring at room temperature for 1 day, all the volatiles were removed *in vacuo*. The solid residue was extracted with toluene and then filtered. Concentration of the filtrate afforded the yellow crystalline Yb(m) triamide [YbL₃] (9). Yield: 0.16 g, 0.16 mmol (16%).

Reaction of [YbL_2(THF)_2] (5) with PhSeSePh. Complex 5 was reacted with PhSeSePh according to a similar procedure as described above, yielding complex **9** as the only isolable product. Reagents used: $[YbL_2(THF)_2]$ (5), 1.59 g, 1.87 mmol; PhSeSePh, 0.29 g, 0.92 mmol. Yield: 0.21 g, 0.22 mmol (23%).

Reaction of [YbL_2(THF)_2] (5) with PhTeTePh. Complex 5 was reacted with PhTeTePh according to a similar procedure as described above, yielding complex 9 as the only isolable product. Reagents used: $[YbL_2(THF)_2]$ (5), 1.59 g, 1.87 mmol; PhTeTePh, 0.38 g, 0.94 mmol. Yield: 0.12 g, 0.12 mmol (13%).

X-Ray crystallographic analysis

Single crystals of complexes 2 and 4–9 suitable for X-ray diffraction studies were mounted on glass capillaries and sealed under nitrogen. Data were collected on a Bruker SMART CCD diffractometer or a Bruker KAPPA APEX II diffractometer with graphite-monochromatized Mo K_a radiation ($\lambda = 0.71073$ Å) at 173 K (for 2) and 293–296 K (for 4–9). An empirical absorption correction was applied using the SADABS programme.⁴⁵ The structures were solved by direct phase determination using the computer program SHELX-97 and refined by full-matrix least squares with anisotropic thermal parameters for the non-hydrogen atoms.⁴⁶ Hydrogen atoms were introduced in their idealized positions and included in structure factor calculations with assigned isotropic temperature factors. Details of the data collection and crystallographic data are given in Table 1.^{47,48}

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