

Direct Reaction – One Step Route to Synthesize Lanthanoid-iodide Formamidates**

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Abstract: This paper describes a novel and simple method – direct reaction of lanthanoid metals with equimolar amounts of iodine and a formamidine under ultrasonication as an effective, metal-based route to lanthanoid(III) diiodide formamidates, namely I. *N,N'*-Bis(2,6-diisopropylphenyl)formamidinatodiiodidolanthanoid(III) complexes [Ln(DippForm)₂(thf)₃] (Ln = La, 1, Ce, 2, Tb, 3, Ho, 4, Er, 5, Tm, 6); II. *N,N'*-Bis(2,6-diethylphenyl)formamidinatodiiodidolanthanoid(III) complexes [Ln(EtForm)₂(thf)₃] (Ln = Ce, 7, Nd, 8, Gd, 9, Tb, 10, Dy, 11, Ho, 12, Er, 13, Lu, 14). III. *N,N'*-bis(2,6-dimethylphenyl)formamidinatodiiodidolanthanoid(III) complexes [Ln(XylForm)₂(thf)₃] (Ln = Ce, 15, Nd, 16, Gd, 17, Tm, 18, Lu 19); IV. *N,N'*-bis(phenyl)formamidinatodiiodidolanthanoid complexes [Ln(PhForm)₂(thf)₃] (Ln = Nd, 20, Gd, 21, Er, 22).

Compound [Ce(XylForm)₂I(thf)₂] (23) was also synthesized by the same method except the ratio of I₂ to XylFormH was 1:4. Divalent *N,N'*-bis(2,6-diisopropylphenyl)formamidinato-iodido-lanthanoid(II) complexes [Eu(DippForm)I(thf)₄]·thf (24), [Yb(DippForm)I(thf)₃]·2DippFormH (25), [Sm(DippForm)I(thf)₄]·thf (26) have also been synthesized by direct reactions of the free metals, iodine and DippFormH. Interestingly, [Sm(DippForm)I₂(thf)₃] (27) was obtained by the oxidation of [Sm(DippForm)I(thf)₄]·thf (26) on exposure to air. *N,N'*-Bis(2,6-dimethylphenyl)formamidinatoiodidosamarium(II) [Sm(XylForm)I(thf)₃]_n (28) was also prepared by direct reaction of Sm, iodine and XylFormH (mole ratio of I₂: XylFormH = 1:2). All products have been identified by X-ray crystallography and all the trivalent complexes [Ln(Form)_n]_{3-n} (n = 1 or 2) are stable to rearrangement.

Introduction

Reactive heteroleptic lanthanoid(III) complexes, including hydrides, amides, alkoxides, aryloxides, and cyclopentadienyls have usually been synthesized from LnLX₂ or LnL₂X (L = anionic ligand, X = halide) complexes by metathesis reactions (Scheme 1).^[1–6] The reactants [Ln(L)_nX_{3-n}] (X = Cl, Br, I) have usually been prepared by metathesis reactions with stoichiometric modification (Scheme 2, eq. (1)).^[7–8] However, metathesis syntheses of [Ln(L)_nX_{3-n}] (n = 1 or 2) compounds have potential rearrangement outcomes (Scheme 2, eq. (2)). Rearrangement reactions between LnL₃ and LnX₃ complexes provide another general approach but are subject to similar rearrangement issues (Scheme 2, eq. (3)) with the low solubility of LnCl₃ species inhibiting successful outcomes.^[6b] The Dolgoplosk group and co-workers have successfully synthesised trivalent lanthanoid complexes [(Ph₃C)₂LnCl], [(Ph₃C)LnCl₂], and the sesquichloride

complex [(Ph₃C)₃Ln₂Cl₃] (Ln = Pr³⁺, Nd³⁺, Gd³⁺ and Ho³⁺) employing lanthanoid metals and triphenylmethyl chloride, but the products underwent rearrangement and no crystal structures were reported.^[9]

To prepare divalent heteroleptic lanthanoid complexes [LnL(L')], pseudo-Grignard reagents “RLnI” are a potential starting point and can be prepared by the reaction of organic iodides with lanthanoid metals.^[10] However most attention has been given to their unique reducing properties and their alkylation/arylation capacity.^[11–14] Limited crystallographic characterization of such species has been performed by utilising bulky ligands.^[14] Divalent lanthanoid-iodide pyrazolates [LnPh₂pzl(thf)₄] (Ln = Eu, Yb),^[15] and lanthanoid-iodide formamidates [Ln(Form)_n]_{3-n} (n = 1 or 2) (Ln = Eu, Yb) (FormH = XylFormH, MesFormH and DippFormH (ArNCHNAr; Ar = 2,6-Me₂C₆H₃, 2,4,6-Me₃C₆H₂, and 2,6-iPr₂C₆H₃)^[16] have been prepared by the sonication of lanthanoid metal with iodobenzene, followed by the addition of a trapping proligand (pzH or FormH), but all the reported complexes were limited to those of the divalent favouring lanthanoids Eu/Yb, and the lanthanoid formamidates were obtained in low yields owing to Schlenk equilibrium and (for Yb) oxidation to Ln^{III}.

Lanthanoid complexes have been successfully prepared by direct reaction of rare earth metals and protic agents (for example 3,5-disubstituted pyrazoles, pyrazolones, 2,6-diisopropylphenol and other phenols) with small amount of iodine as an activation catalyst (Scheme 3, eq. (1)).^[17] This method provides encouragement to extend the applicability of iodine activated Ln metals in synthesis. Initially, the aim of this work was to synthesize lanthanoid formamidates [Ln(ArForm)₃] by direct reaction of iodine activated Ln metals and formamidines, but [Ln(ArForm)₂I] complexes were also obtained with low

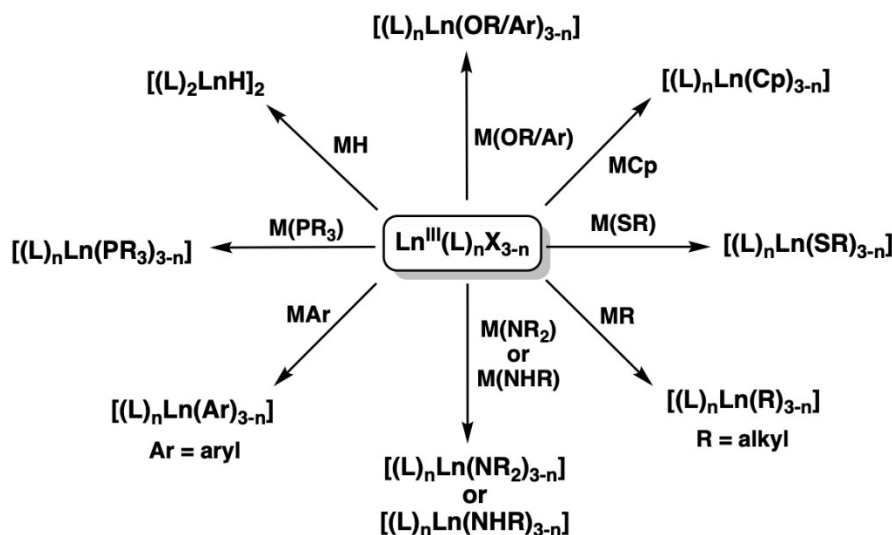
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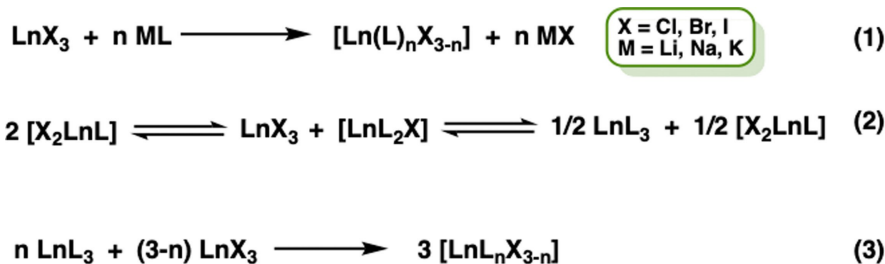
[**] We dedicate this paper to Professor Frank T. Edelmann of Otto-von-Guericke-Universität Magdeburg in recognition of his major contribution to rare earth chemistry and for his valuable help to other workers in the field with his annual reviews of progress in the area.

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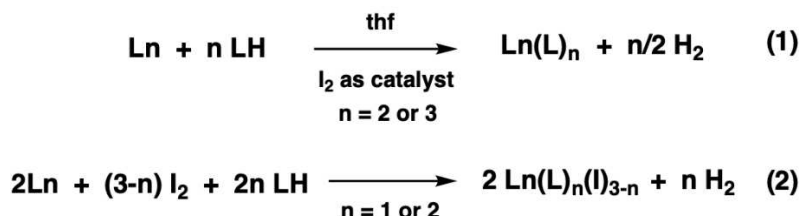
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Scheme 1. Heteroleptic lanthanoid metal-organic compounds synthesized from $[\text{Ln}^{\text{III}}(\text{L})_n\text{X}_{3-n}]$.



Scheme 2. Metathesis syntheses and potential rearrangement of $[\text{Ln}(\text{L})_n\text{X}_{3-n}]$.



Scheme 3. Synthesis of lanthanoid complexes with I_2 .

yields in addition to $[\text{Ln}(\text{ArForm})_3]$.^[18] Hence, it appeared possible to exploit this observation and synthesize $[\text{Ln}(\text{ArForm})_n\text{I}_{3-n}]$ complexes on a preparative scale (Scheme 3, eq. (2)). These are potentially valuable synthons for a wide range of heteroleptic complexes, such as hydrides, organometallics, cyclopentadienyls, organoamides, and organo-oxides, etc. (Scheme 1, $\text{X} = \text{I}$)

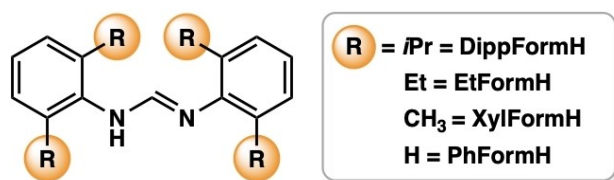
Recently we presented a preliminary report that this simple method gave a number of trivalent lanthanoid formamidates $[\text{Ln}(\text{ArForm})_n\text{I}_{3-n}]$ ($\text{ArForm} = N,N'$ -bis(2,6-difluorophenyl)formamidate (DFForm), or N,N' -bis(2,6-diisopropylphenyl)formamidate (DippForm)) in reasonable yields.^[19] For the less bulky DFFormH, the stoichiometry $n = 1$ or 2 can be controlled by employing different ratios of iodine and DFFormH, but the bulkier DippFormH gave only diiodides. For

Eu and Yb, the heteroleptic $[\text{Ln}(\text{DFForm})\text{I}]$ was obtained together with the Schlenk equilibrium products, $[\text{Ln}(\text{DFForm})_2]$, and $[\text{LnI}_2]$. This paper examines the generality of the direct reaction of Ln, I_2 and different formamidines to afford new $[\text{Ln}(\text{ArForm})_n\text{I}_{3-n}]$ ($\text{ArForm} = \text{DippForm}, \text{EtForm}, \text{XylForm}, \text{PhForm}$ Scheme 4) complexes in good yields.

Results and discussion

Synthesis of formamidatiodiolanthanoid(III) complexes

The N,N' -bis(2,6-diisopropylphenyl)formamidatiodiolanthanoid(III) complexes, $[\text{La}(\text{DippForm})_2(\text{thf})_3] \cdot 0.5 \text{thf}$ **1**, $[\text{Ce}$



Scheme 4. *N,N'*-Bis(aryl)formamidine (ArFormH) proligands used in this paper.

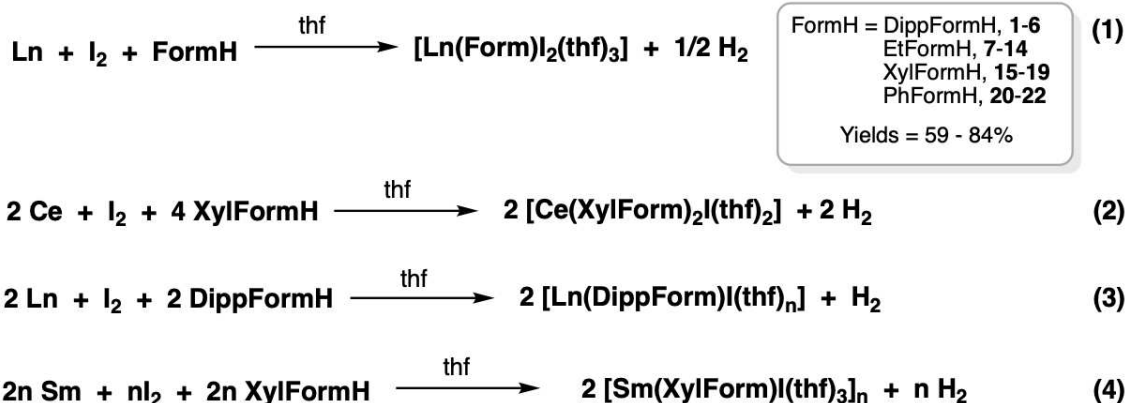
(DippForm)₂(thf)₃·0.5thf **2**, [Tb(DippForm)₂(thf)₃·0.5thf **3**, [Ho(DippForm)₂(thf)₃·0.5thf **4**, [Er(DippForm)₂(thf)₃·2thf **5** and [Tm(DippForm)₂(thf)₃·0.5thf **6**, *N,N'*-bis(2,6-diethylphenyl)formamidinatodiodidolanthanoid complexes [Ln(EtForm)₂(thf)₃·thf (Ln = Ce, **7**, Nd, **8**, Gd, **9**, Tb, **10**, Dy, **11**, Ho, **12**, Er, **13**, Lu, **14**), *N,N'*-bis(2,6-dimethylphenyl)formamidinatodiodidolanthanoid complexes, [Ce(XylForm)₂(thf)₃·1.5thf **15**, [Nd(XylForm)₂(thf)₃·thf **16**, [Gd(XylForm)₂(thf)₃·thf **17**, [Tm(XylForm)₂(thf)₃·thf **18**, and [Lu(XylForm)₂(thf)₃·thf **19**, and *N,N'*-bis(diphenyl)formamidinatodiodidolanthanoid complexes [Ln(PhForm)₂(thf)₃] (Ln = Nd, **20**, Gd, **21**, Er, **22**) were prepared by direct reactions between an excess of lanthanoid metal, iodine and the corresponding pro-ligand FormH (DippFormH, EtFormH, XylFormH, and PhFormH) (mole ratio of I₂: FormH = 1:1) in thf on ultrasonication (Scheme 5, eq. (1)). This greatly extends the scope of the synthetic method from the examples [Ln(DippForm)₂(thf)₃] (Ln = Nd, Gd, Dy, Lu) of our preliminary report.^[19] For the bulky ligand DippFormH, the reaction was complete in one week, while all other subjected ligands required only three days. Compound [Ce(XylForm)₂(thf)₂·2.25thf **23** was also synthesized by the same method except the ratio of I₂ to XylFormH was 1:4 (Scheme 5, eq. (2)). As **15** and **23** were prepared successfully, both reactions (Scheme 5, eq. (1) and (2)) can work with the same metal. However, the synthesis of [Ln(XylForm)₂] failed for the smaller metals Gd and Tm with [Ln(XylForm)₂] isolated instead. Likewise an attempt to prepare [Ce(EtForm)₂] for the bulkier Form ligand furnished [Ce(EtForm)₂]·2thf, a different solvate from

complex **7**. So far [Ln(Form)₂] complexes are only generally accessible for the smaller DFForm.^[19] Single crystals of the trivalent complexes [Ln(DippForm)₂(thf)₃] (**1–4**, and **6**) have the same composition as the reported [Ln(DippForm)₂(thf)₃] (Ln = Nd, Gd, Dy, Lu), previously characterized as mono(thf) solvates.^[19]

Good yields (based on the FormH ligands) of crystalline products were obtained from the concentrated filtrates. Complexes **1–23** were characterized by single crystal X-ray diffraction and the bulk samples by metal analysis after problems with some microanalyses. These were close to the values expected for the compositions found by X-ray crystallography or to values corresponding to loss of lattice/coordinated thf solvent (see below). Appropriate ¹H NMR spectra were obtained for diamagnetic **1**, **14**, and **19** (Figure S1, S4, S6) and paramagnetic **7**, **8**, **15**, and **12** (Figure S2, S3, S5), but again with loss of thf in some cases. Infrared spectra (see experimental section) showed features expected for the Form ligands together with ring stretching C–O bands of coordinated thf^[20] at *ca.* 1010 and 870–850 cm⁻¹.

Synthesis of formamidinatoiodidolanthanoid(II) complexes

N,N'-Bis(2,6-diisopropylphenyl)formamidinatoiodidolanthanoid(II) complexes [Eu(DippForm)I(thf)₄]·thf **24**, [Yb(DippForm)I(thf)₃]·2DippFormH **25** and [Sm(DippForm)I(thf)₄]·thf **26** were also prepared by direct reactions of the free metals, iodine and DippFormH (mole ratio of I₂: DippFormH = 1:2) on ultrasonication for three days (Scheme 5 eq. (3)). Crystalline products were obtained by evaporation of the filtrates under vacuum. For Sm, the trivalent compound [Sm(DippForm)₂(thf)₃]·0.5thf **27** was obtained by the oxidation of divalent [Sm(DippForm)I(thf)₄] **26** on brief exposure to air. A co-product must be formed, e.g. Sm(DippForm)O, but only single crystals of **27** were identified. The extreme sensitivity to oxygen of **26** is shown by an attempted visible/near infrared spectrum obtained under inert atmosphere conditions, since this showed features of Sm^{II} (**26**)^[21a] and Sm^{III} (**27**)^[21b-e] (Experimental section), despite the



Scheme 5. Synthesis of formamidinatoiodidolanthanoids.

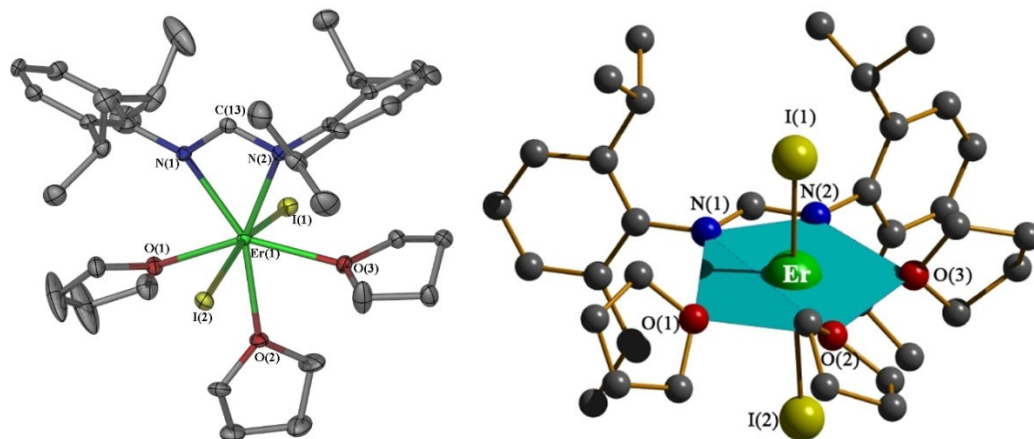


Figure 1. Molecular structure of $[\text{Er}(\text{DippForm})\text{I}_2(\text{thf})_3]$ (representative of La, 1, Ce, 2, Tb, 3, Ho, 4, Er, 5, Tm, 6, Sm, 27) with non-hydrogen atoms represented by 50% thermal ellipsoids. The lattice thf molecules and hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°) for 5 Er–N(1) 2.395(2), Er–N(2) 2.366(2), Er–O(1) 2.3905(19), Er–O(2) 2.4458(19), Er–O(3) 2.384(2), Er–I(1) 3.0107(2), Er–I(2) 3.0044(2), O(1)–Er–O(2) 74.00(7), O(1)–Er–O(3) 147.25(7), O(2)–Er–O(3) 73.40(7), I(1)–Er–I(2) 165.565(7), C(13)–Er–I(1) 99.99(6), C(13)–Er–I(2) 94.44(6).

solution having the deep blue colour characteristic of **26** (see picture in Figure S7). The multiple bands in the near infrared region are as expected for Sm^{III} .^[21b–e] Complex $[\text{Yb}(\text{DippForm})\text{I}(\text{thf})_3] \cdot 2\text{DippFormH}$ **25**, previously obtained as a mono(tetrahydrofuran) solvate $[\text{Yb}(\text{DippForm})\text{I}(\text{thf})_3] \cdot \text{thf}$,^[16] has now been obtained with free pro-ligand of crystallization. Complex $[\text{Eu}(\text{DippForm})\text{I}(\text{thf})_4] \cdot \text{thf}$ **24** has been previously observed and reported.^[16] The *N,N'*-bis(2,6-dimethylphenyl)formamidinatioiodidolanthanoid(II) complex $[\text{Sm}(\text{XylForm})\text{I}(\text{thf})_3]_n$ **28** was also prepared by direct reaction of Sm metal, iodine and XylFormH (mole ratio of I_2 : XylFormH = 1:2) (Scheme 5, eq. (4)).

Molecular structures

Representative structures of **1–28** are shown in Figures 1–6, which also list selected bond angles (°) and lengths (Å). Additional structural metrics are available in the SI.

Complexes $[\text{Ln}(\text{DippForm})\text{I}_2(\text{thf})_3]$ (1–6 and 27)

All $[\text{Ln}(\text{DippForm})\text{I}_2(\text{thf})_3]$ (Ln = La, 1, Ce, 2, Tb, 3, Ho, 4, Er, 5, Tm, 6, Sm, 27) complexes, **1–4**, **6** and **27** crystallize in the orthorhombic space group *Pbca*, and are isomorphs of $[\text{Ln}(\text{DippForm})\text{I}_2(\text{thf})_3] \cdot \text{thf}$ (Ln = Nd, Gd, Dy)^[19] despite lattice solvent differences. Only complex **5** crystallized in the triclinic space group *P-1*, and is an isomorph of $[\text{Lu}(\text{DippForm})\text{I}_2(\text{thf})_3] \cdot 2\text{thf}$.^[19] The complexes are monomeric and the Ln atoms are found to be seven coordinate at the centre of a pentagonal bipyramid, with one chelating DippForm ligand, two *transoid* iodide ligands, and three thf ligands (Figure 1). The I(1)–Ln–I(2) angles are from 165.565(7)–167.58(2)°, displaying a near linear coordination of the negatively charged donor atoms. Three O atoms (from thf) in a *mer* array and two N atoms are in the equatorial plane with Ln^{III} (Figure 1 RHS). The iodide ligands are *cisoid* to

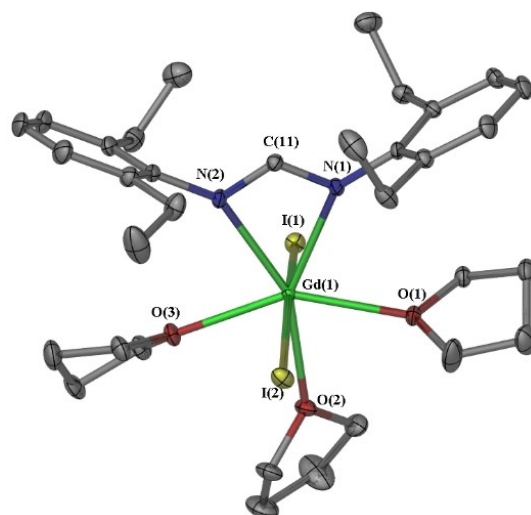


Figure 2. Molecular structure of $[\text{Gd}(\text{EtForm})\text{I}_2(\text{thf})_3]$ (representative of Ce, 7, Nd, 8, Gd, 9, Tb, 10, Dy, 11, Ho, 12, Er, 13, Lu, 14) with non-hydrogen atoms represented by 50% thermal ellipsoids. Selected bond lengths (Å) and angles (°) 9 Gd–N(1) 2.4216(16), Gd–N(2) 2.4244(16), Gd–O(1) 2.4353(14), Gd–O(2) 2.4627(14), Gd–O(3) 2.4231(14), Gd–I(1) 3.04992(17), Gd–I(2) 3.04930(17), O(1)–Gd–O(2) 73.38(5), O(1)–Gd–O(3) 149.11(5), O(2)–Gd–O(3) 75.92(5), I(1)–Gd–I(2) 166.490(5), C(11)–Gd–I(1) 97.234, C(11)–Gd–I(2) 96.215.

the DippForm ligand (I(1)–Ln–C(13) and I(2)–Ln–C(13) are 94–100°). The average Ln–N bond lengths for **1–6**, and **27** are 2.52 (2.524(3) and 2.514(3)), 2.50 (2.493(10) and 2.498(11)), 2.41 (2.407(3) and 2.412(3)), 2.39 (2.391(7) and 2.392(8)), 2.38 (2.395(2) and 2.366(2)), 2.37 (2.371(4) and 2.364(4)) and 2.44 (2.438(6) and 2.435(6)) Å respectively, and the average Ln–I bond lengths for **1–6**, and **27** are 3.17 (3.1676(4) and 3.1684(4)), 3.15 (3.1451(13) and 3.1462(13)), 3.04 (3.0369(4) and 3.0514(3)), 3.03 (2.991(10) and 3.059(3)), 3.01 (3.0107(2) and 3.0044(2)), 3.00 (3.0081(5) and 2.9935(5)) and 3.10 (3.0877(7) and 3.110(4)) Å respectively, with the sequential decreases being consistent with the lanthanoid contraction.

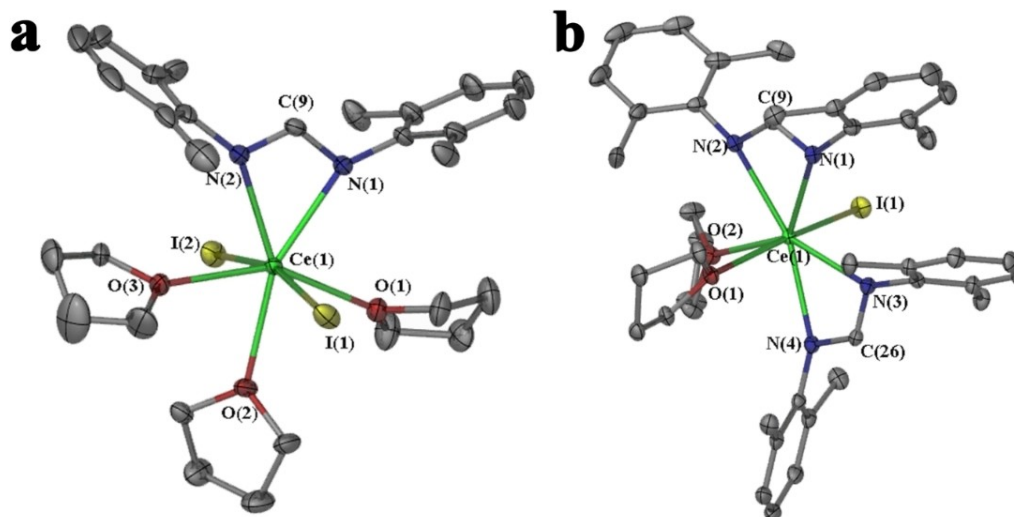


Figure 3. Molecular structure of (a) $[\text{Ce}(\text{XylForm})\text{I}_2(\text{thf})_3]$ (representative of Ce, 15, Nd, 16, Gd, 17, Tm, 18, Lu, 19) and (b) $[\text{Ce}(\text{XylForm})_2\text{I}(\text{thf})_2]$ **23** with non-hydrogen atoms represented by 50% thermal ellipsoids. Selected bond lengths (Å) and angles ($^\circ$) **15** Ce–N(1) 2.493(3), Ce–N(2) 2.486(3), Ce–O(1) 2.496(2), Ce–O(2) 2.570(2), Ce–O(3) 2.496(2), Ce–I(1) 3.1359(3), Ce–I(2) 3.1449(3), O(1)–Ce–O(2) 77.33(8), O(1)–Ce–O(3) 150.18(8), O(2)–Ce–O(3) 72.89(8), I(1)–Ce–I(2) 165.53(3), C(9)–Ce–I(1) 98.59(7), C(9)–Ce–I(2) 95.88(7); **23** Ce–N(1) 2.538(2), Ce–N(2) 2.543(2), Ce–N(3) 2.478(2), Ce–N(4) 2.575(2), Ce–O(1) 2.532(2), Ce–O(2) 2.574(2), Ce–I(1) 3.1379(6), O(1)–Ce–I(1) 162.09(5), O(2)–Ce–I(1) 82.71(5), O(1)–Ce–O(2) 80.18(7), C(9)–Ce–C(26) 136.79(8).

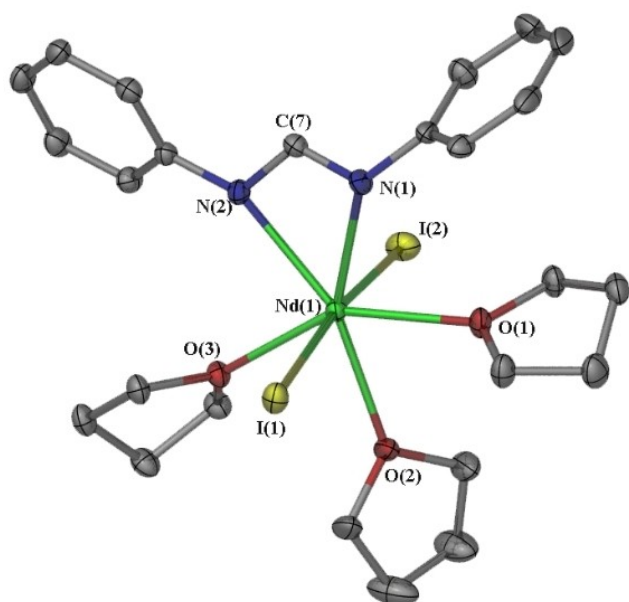


Figure 4. Molecular structure of $[\text{Nd}(\text{PhForm})\text{I}_2(\text{thf})_3]$ (representative of Nd, **20**, Gd, **21**, Er, **22**) with non-hydrogen atoms represented by 50% thermal ellipsoids. Selected bond lengths (Å) and angles ($^\circ$) **20** Nd–N(1) 2.440(3), Nd–N(2) 2.492(3), Nd–O(1) 2.483(3), Nd–O(2) 2.505(3), Nd–O(3) 2.456(2), Nd–I(1) 3.0929(6), Nd–I(2) 3.1061(6), O(1)–Nd–O(2) 72.55(10), O(1)–Nd–O(3) 147.91(9), O(2)–Nd–O(3) 75.37(9), I(1)–Nd–I(2) 171.982(9), C(7)–Nd–I(1) 99.01(8), C(7)–Nd–I(2) 88.99(8).

Complexes $[\text{Ln}(\text{EtForm})\text{I}_2(\text{thf})_3]$ (7–14)

All $[\text{Ln}(\text{EtForm})\text{I}_2(\text{thf})_3]\cdot\text{thf}$ complexes (7–14) crystallize in the triclinic space group $P-1$. The Ln^{3+} ion is monomeric and seven coordinate, with one chelating EtForm ligand, two *transoid* iodide ligands (e.g. I(1)–Gd–I(2) 166.490(5) $^\circ$; range 166.024(10) to 167.054(6) $^\circ$), and three *mer* thf ligands (Figure 2). The Ln^{3+}

ion possesses a distorted pentagonal bipyramidal coordination with three O atoms and two N atoms in the equatorial plane. The average Ln–N, Ln–O, and Ln–I bond lengths for 7–14 (see SI section 1.2) are consistent with the lanthanoid contraction.

Complexes $[\text{Ln}(\text{XylForm})\text{I}_2(\text{thf})_3]$ (15–19 and 23)

All $[\text{Ln}(\text{XylForm})\text{I}_2(\text{thf})_3]$ complexes (15–19) crystallize in the monoclinic space group $C2/c$. The Ln^{3+} ion in 15–19 is monomeric and seven coordinate, with one chelating XylForm ligand, two *transoid* iodide ligands (I(1)–Ln–I(2) 164.12(14) to 172.90(8) $^\circ$), and three thf ligands (Figure 3a). The Ln^{3+} ion possesses a distorted pentagonal bipyramidal coordination sphere, which is similar to complexes 1–14 and the reported $[\text{Ln}(\text{ArForm})\text{I}_2(\text{thf})_3]$ (ArForm = DFForm or DippForm).^[19] The I(1)–Ln–I(2) bond angles are close to linear. The average Ln–N, Ln–O, and Ln–I bond lengths for 15–19 are consistent with the lanthanoid contraction. The X-ray crystal structure of $[\text{Ce}(\text{XylForm})_2\text{I}(\text{thf})_2]$ **23** reveals a monomeric and seven coordinate complex, comprising two chelating XylForm ligands (C9–Ln–C26 136.79(8) $^\circ$), one terminal iodide ligand, and two *cis* thf ligands (O1–Ce–O2 80.18(7) $^\circ$) (Figure 3b), which is different from $[\text{Ln}(\text{DFForm})_2\text{I}(\text{thf})_2]$ which has two *trans* thf ligands (O1–Ln–O1# from 170 to 172 $^\circ$).^[19]

Complexes $[\text{Ln}(\text{PhForm})\text{I}_2(\text{thf})_3]$ (20–22)

$[\text{Ln}(\text{PhForm})\text{I}_2(\text{thf})_3]$ (Ln = Nd, **20**, Gd, **21**, Er, **22**) crystallize in the monoclinic space group $P2_1/c$ (**20**) and $P2_1/n$ (**21**, **22**). The complexes are monomeric and seven coordinate, with one chelating PhForm ligand, two *transoid* iodide ligands, and three

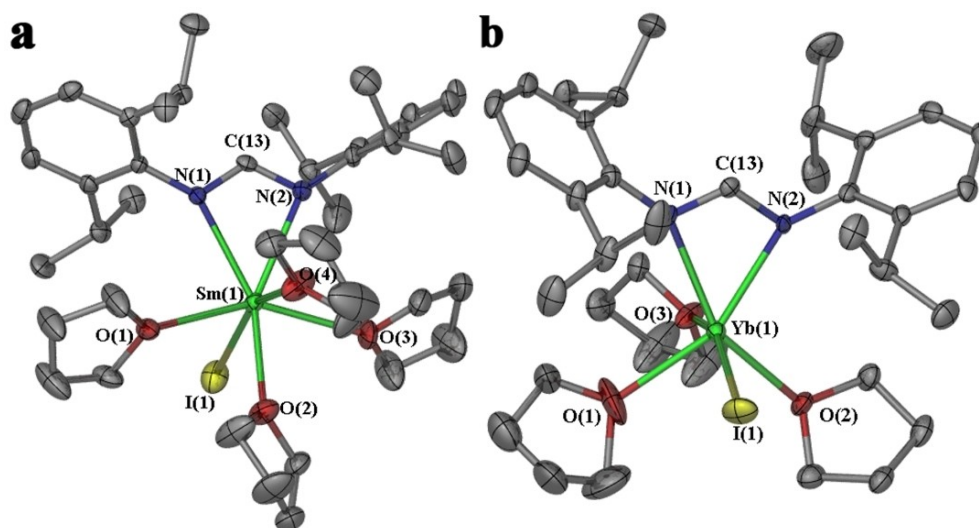


Figure 5. Molecular structure of (a) $[\text{Sm}(\text{DippForm})\text{I}(\text{thf})_4] \cdot \text{thf}$ (representative of Eu, **24**, Sm, **26**) (b) $[\text{Yb}(\text{DippForm})\text{I}(\text{thf})_3] \cdot 2\text{DippFormH}$ (**25**) with non-hydrogen atoms represented by 50% thermal ellipsoids. The lattice thf molecules, DippFormH and hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$) **25** Yb–N(1) 2.466(5), Yb–N(2) 2.463(4), Yb–O(1) 2.443(5), Yb–O(2) 2.416(4), Yb–O(3) 2.449(4), Yb–I(1) 3.1241(4), C(13)–Yb–I(1) 109.93(11), O(1)–Yb–O(2) 101.82(19), O(1)–Yb–O(3) 78.50(19), O(2)–Yb–O(3) 78.76(15), I(1)–Yb–O(1) 86.17(16), I(1)–Yb–O(2) 88.49(10), I(1)–Yb–O(3) 157.49(10), C(13)–Yb–O(1) 129.8(2), C(13)–Yb–O(2) 124.93(15), C(13)–Yb–O(3) 92.57(15); **26** Sm–N(1) 2.598(6), Sm–N(2) 2.642(6), Sm–O(1) 2.570(6), Sm–O(2) 2.612(6), Sm–O(3) 2.632(6), Sm–O(4) 2.600(6), Sm–I(1) 3.2752(10), C(13)–Sm–I(1) 111.44(14), O(1)–Sm–O(2) 72.4(2), O(1)–Sm–O(3) 150.2(8), O(1)–Sm–O(4) 89.1(2), O(2)–Sm–O(3) 78.7(2), O(2)–Sm–O(4) 72.5(2), O(3)–Sm–O(4) 86.3(2), I(1)–Sm–O(1) 90.00(14), I(1)–Sm–O(2) 86.92(15), I(1)–Sm–O(3) 84.09(17), I(1)–Sm–O(4) 158.62(16), C(13)–Sm–O(1) 103.07(19), C(13)–Sm–O(2) 161.3(2), C(13)–Sm–O(3) 105.8(2), C(13)–Sm–O(4) 89.5(2).

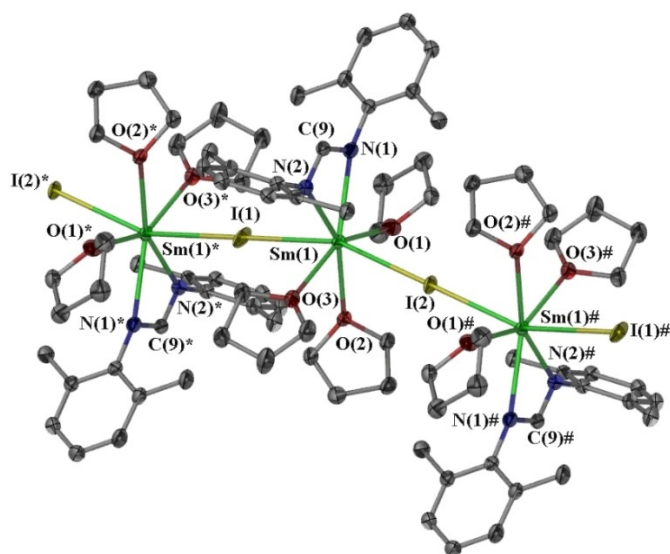


Figure 6. Molecular structure of $[\text{Sm}(\text{XylForm})\text{I}(\text{thf})_3]_n$ (**28**) with non-hydrogen atoms represented by 50% thermal ellipsoids. Selected bond lengths (Å) and angles ($^\circ$) **28** Sm–N(1) 2.637(4), Sm–N(2) 2.565(4), Sm–O(1) 2.583(4), Sm–O(2) 2.641(4), Sm–O(3) 2.621(4), Sm–I(1) 3.2824(8), Sm–I(2) 3.2873(7), O(1)–Sm–O(2) 70.01(12), O(1)–Sm–O(3) 150.64(12), O(2)–Sm–O(3) 83.19(8), I(1)–Sm–I(2) 160.017(11), C(9)–Sm–I(1) 94.59(8), C(9)–Sm–I(2) 104.05(8). Symmetry operators: *1-x, 1-y, 1-z; #1-x, 1-y, 2-z.

thf ligands (Figure 4), and are otherwise similar to the preceding complexes **1–19**.

Overall, the structures of complexes **1–22** have a striking structural similarity to those of $[\text{LnCp}_2(\text{thf})_3]$ (Ln=Sm, Tm),^[22] where a Cp is interchanged for a Form ligand. The average Sm–I and Sm–O bond lengths of $[\text{Sm}(\text{DippForm})\text{I}_2(\text{thf})_3] \cdot 0.5\text{thf}$

27 are 3.10 and 2.47 Å, similar to $[\text{SmCp}_2(\text{thf})_3] < \text{Sm-I} > 3.16 \text{ \AA}$ and $< \text{Sm-O} > 2.46 \text{ \AA}$.^[22a] The average $< \text{Tm-I} >$ bond lengths are 3.00 and 2.99 Å for complexes $[\text{Tm}(\text{DippForm})\text{I}_2(\text{thf})_3] \cdot 0.5\text{thf}$ **6** and $[\text{Tm}(\text{XylForm})\text{I}_2(\text{thf})_3] \cdot \text{thf}$ **18**, and average $< \text{Tm-O} >$ bond lengths are 2.41 and 2.38 Å respectively, which are comparable to $[\text{TmCp}_2(\text{thf})_3] < \text{Tm-I} > 3.09 \text{ \AA}$; $< \text{Tm-O} > 2.36 \text{ \AA}$.^[22b] The longer $< \text{Ln-I} >$ values for the Cp complexes are as expected for the higher formal coordination number (8) compared with 7 for the Form complexes. However the same relationship is not seen for the $< \text{Ln-O} >$ bond lengths which are either similar for Ln=Sm, or longer in the Form complexes for Ln=Tm. Despite the formal coordination number difference, the similarities in the structures support the view that formamidinates can be regarded as N donor alternatives to cyclopentadienyls.

Complexes $[\text{Ln}(\text{DippForm})\text{I}(\text{thf})_n]$ (**24–26**)

Single crystals of $[\text{Ln}(\text{DippForm})\text{I}(\text{thf})_4] \cdot \text{thf}$ (Ln=Eu, **24**, Sm, **26**) are isomorphous, and **24** has unit cell parameters in agreement with the reported X-ray data for $[\text{Eu}(\text{DippForm})\text{I}(\text{thf})_4] \cdot \text{thf}$.^[16] Compounds **24** and **26**, which crystallize in the monoclinic space group $P2_1/c$, are seven coordinate pseudo-octahedral, with one chelating DippForm ligand, one iodide ligand and four molecules of thf (Figure 5a). $[\text{Yb}(\text{DippForm})\text{I}(\text{thf})_3] \cdot 2\text{DippFormH}$ (**25**), solvated with two proligands of crystallization, crystallizes in the monoclinic space group Pc (Figure 5b). The complex is monomeric and the Yb^{2+} ion is six coordinate distorted-octahedral, with one chelating DippForm ligand, one iodide ligand and three thf donors. The structure is similar to that of the reported $[\text{Yb}(\text{DippForm})\text{I}(\text{thf})_3] \cdot \text{thf}$. The reduced coordina-

tion number compared to those of the seven-coordinate Eu (24) and Sm (26) complexes is consistent with the smaller ionic radius of Yb²⁺.^[23] For complexes 24–26, the DippForm ligand and iodide ligand are arranged in a *cisoid* fashion [C(13)–Yb–I(1) 109.93(11)°, C(13)–Sm–I(1) 111.44(14)°]. The average Ln–N bond lengths are 2.47 Å (2.466(5) and 2.463(4)) for Yb 25 [2.43 Å in [Yb(DippForm)(thf)₃]·thf], and 2.62 Å (2.598(6) and 2.642(6)) for Sm 26, and 2.60 Å for the reported [Eu(DippForm)I(thf)₄]·thf.^[16] The Ln–I bond length is 3.1241(4) Å for Yb [3.05 Å in [Yb(DippForm)(thf)₃]·thf], 3.2752(10) Å for Sm, and 3.26 Å for reported [Eu(DippForm)I(thf)₄]·thf,^[16] respectively, which are consistent with the lanthanoid ion radii differences.

Complex [Sm(XylForm)I(thf)₃]_n 28

The polymeric compound [Sm(XylForm)I(thf)₃]_n 28 crystallizes in the triclinic space group *P*-1, and has seven coordinate pseudo-octahedral stereochemistry for the Sm²⁺ ions, with one chelating XylForm ligand, two *transoid* iodide ligands (I(1)–Sm–I(2) 160.017(11)°), and three thf donors (Figure 6). The XylForm ligand and the iodide ligands are arranged in a *cisoid* fashion [C(9)–Sm–I(1) 94.59(8), C(9)–Sm–I(2) 104.05(8)]. The [Sm(XylForm)I(thf)₃] units are bridged by the I1 and I2 atoms, and each unit is inverted by the symmetry code: *1-x,1-y,1-z and #1-x,1-y,2-z. Compared to the divalent [Sm(DippForm)I(thf)₄] with a terminal I atom, the less bulky XylForm forms a polymer with one more coordinated I, but one less thf molecule. This change reduces steric crowding.^[24]

Conclusions

A simple reaction between free lanthanoid metals, iodine, and formamidines (FormH) provides a convenient high yield synthesis of multiple [Ln(Form)₂(thf)₃] (Form = DippForm, EtForm, XylForm, PhForm) complexes 1–23, thereby establishing the generality of the method. The products are stable to rearrangement, hence are potential reagents to access a wide variety of heteroleptic lanthanoid formamidates [Ln(Form)X₂] (e.g. X = R, OAr, Cp, NR₂ etc). All are seven coordinate monomers with *transoid* iodides with a structural similarity to the corresponding cyclopentadienyls, supporting the potential of formamidates as N-donor alternatives to Cps. Attempts to obtain [Ln(Form)₂-(thf)_n] by stoichiometric modification of the synthesis were much less successful implying a steric block in the synthesis. The method was also adapted to give Ln^{II}(Form)I (Ln = Sm, Eu, Yb) 24–26 complexes but the samarium(II) derivatives were exceptionally air sensitive. [Sm^{II}(XylForm)I(thf)₃]_n is a novel iodide bridged polymer contrasting the monomeric structure for similarly crystallised [Sm(DippForm)I(thf)₄].

Experimental

General

The lanthanoid compounds described here are highly air- and moisture-sensitive, hence they were prepared and handled using vacuum-nitrogen line techniques and a dry box under an atmosphere of purified nitrogen. All formamidines were prepared by reported literature methods.^[25] Lanthanoid metals were purchased from Santoku/Molycorp/Eutectix. Large chunks of the representative Ln metals were filed in the drybox before use. All other reagents were purchased from Sigma and used without purification. Solvents (thf, toluene and C₆D₆) were pre-dried by distillation over sodium or sodium benzophenone ketyl before being stored under an atmosphere of nitrogen over 3 Å molecular sieves. IR spectra were recorded as Nujol mulls between NaCl plates using an Agilent Technologies Cary 630 FTIR or a Perkin Elmer 1600 Series FTIR instrument within the range 4000–700 cm⁻¹. UV-Vis-NIR spectra were collected as solution in a J. Young valve quartz cell (1 mm) on a Cary 5G UV-Vis-NIR Spectrophotometer. ¹H NMR spectra were recorded with a Bruker 400 MHz spectrometer. Microanalyses were determined by the Elemental Analysis Service, London Metropolitan University, with all samples sealed in tubes under nitrogen. The metal analyses were carried out after decomposition of the sample with dilute HCl, buffering and complexometric titration with Na₂H₂(edta) and Xylenol Orange indicator. Melting points were determined in sealed glass capillaries under nitrogen and are uncalibrated. Crystals were measured on a Rigaku SynergyS diffractometer or at the Australian Synchrotron on the MX1 macromolecular beamlines. Crystal data and refinement details are given in Table S1. CCDC 2255902–2255924 for compounds 1–23, 2255925–2255928 for compounds 25–28, contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre (CCDC) via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of formamidinatoiodidolanthanoid(III) complexes

General procedure for 1–22

Lanthanoid metal powder (1.0 mmol), iodine (0.25 mmol), Dipp-FormH/ EtFormH/XylFormH/PhFormH (0.25 mmol) and dry THF (10 ml) were placed in a Schlenk flask in a nitrogen-filled dry box. The mixture was ultrasonicated for one week. The reaction mixture was filtered. Crystals were obtained after the filtrate was evaporated to half volume under vacuum.

[La(DippForm)I₂(thf)₃]·0.5 thf 1

Colourless crystals (0.164 g, 63%), M.p. > 300 °C. (Found: La, 14.36%; C₃₉H₆₃I₂LaN₂O_{3.5} (1008.62) requires La, 13.77%, loss of 0.5 thf of crystallisation, C₃₇H₅₉I₂LaN₂O₃ (972.59) requires La, 14.28%). IR (crystal oil): 1666 m, 1589 m, 1528 s, 1325 s, 1276 s, 1181 s, 1106 s, 1062 s, 1018vs, 936 s, 911 s, 885 s, 801 s, 770s, 753 m 716 cm⁻¹. ¹H NMR (400 MHz, C₆D₆, ppm): 8.51 (s, 1H, NCHN), 7.19–7.05 (m, 6H, H(3,4,5)), 4.27 (m, 4H, CH), 3.83 (m, 14H, thf), 1.52–1.32 (m, 24H, CH₃), 1.24 (m, 14H, thf).

[Ce(DippForm)I₂(thf)₃]·0.5 thf 2

Colourless crystals (0.148 g, 59%), decomposed 200 °C. (Found: Ce, 14.42%; C₃₉H₆₃CeI₂N₂O_{3.5} (1009.83) requires Ce, 13.87%, loss of 0.5 thf of crystallisation, C₃₇H₅₉CeI₂N₂O₃ (973.80) requires Ce, 14.39%). IR

(crystal oil): 1665 m, 1592 m, 1521 s, 1319 s, 1270s, 1191 s, 1100 s, 1066 s, 1017vs, 944 m, 914 m, 863 s, 804 s, 760s, 724 m cm⁻¹.

[Tb(DippForm)I₂(thf)₃] · 0.5 thf 3

Colourless crystals (0.179 g, 70%), M.p. 234–236 °C. (Found: Tb, 16.28%; C₃₉H₆₃I₂N₂O_{3.5}Tb (1028.63) requires Tb, 15.45%, loss of 0.5 thf of crystallisation, C₃₇H₅₉I₂N₂O₃Tb (992.61) requires Tb, 16.01%). IR (crystal oil): 1666 m, 1592 m, 1525 s, 1320s, 1272 s, 1192 s, 1102 s, 1067 s, 1019vs, 948 m, 916 m, 864 s, 805 s, 762 s, 724 m cm⁻¹.

[Ho(DippForm)I₂(thf)₃] · 0.5 thf 4

Pink crystals (0.164 g, 66%), M.p. 242–244 °C. (Found: Ho, 16.36%; C₃₉H₆₃HoI₂N₂O_{3.5} (1034.64) requires Ho, 15.94%, loss of 0.5 thf of crystallisation, C₃₇H₅₉HoI₂N₂O₃ (998.61) requires Ho, 16.52%). IR (Nujol): 1666 m, 1593 m, 1524 s, 1320 m, 1272 m, 1192 s, 1101 m, 1069 s, 1017vs, 935 m, 916 m, 863 s, 804 s, 774 s, 760s, 723 m cm⁻¹.

[Er(DippForm)I₂(thf)₃] · 2 thf 5

Pink crystals (0.232 g, 81%), M.p. 246–248 °C. (Found: C, 38.35; H, 5.40; N, 3.51; C₄₅H₇₅ErI₂N₂O₅ (1145.13), loss of five thf, C₂₅H₃₅ErI₂N₂ (784.63) requires C, 38.27; H, 4.50; N, 3.57%). IR (Nujol): 1669 m, 1587 w, 1525 m, 1334 w, 1297 m, 1272 m, 1235 w, 1189 s, 1159 w, 1097 m, 1075 s, 1030vs, 935 m, 919 w, 863 m, 824 m, 799 s, 756 s, 722 s cm⁻¹.

[Tm(DippForm)I₂(thf)₃] · 0.5 thf 6

Colourless crystals (0.205 g, 79%), M.p. 260–262 °C. (Found: Tm, 17.00%; C₃₉H₆₃I₂N₂O_{3.5}Tm (1038.64) requires Tm, 16.26%, loss of 0.5 thf of crystallisation, C₃₇H₅₉I₂N₂O₃Tm (1002.62) requires Tm, 16.85%). IR (crystal oil): 1667 m, 1593 m, 1523 s, 1321 s, 1273 s, 1193 s, 1101 s, 1068 s, 1018vs, 944 m, 916 m, 865 s, 805 s, 761 s, 723 m cm⁻¹.

[Ce(EtForm)I₂(thf)₃] · thf 7

Yellow crystals (0.186 g, 75%), M.p. 206–208 °C. (Found: Ce, 14.28%; C₃₇H₅₉CeI₂N₂O₄ (989.78) requires Ce, 14.16%). IR (Nujol): 1667 s, 1592 w, 1302 w, 1277 w, 1170 w, 1077 m, 1010 w, 968 w, 917 w, 892 w, 852 w, 774 w, 723 s cm⁻¹. ¹H NMR (400 MHz, C₆D₆, ppm): δ = 26.05 ppm (1H; NC(H)N), 8.23 (4H; CH, Ar), 7.76 (2H; CH, Ar), 2.61 (8H; CH₂), 1.50 (12H; CH₃).

[Nd(EtForm)I₂(thf)₃] · thf 8

Purple crystals (0.196 g, 79%), M.p. 205–208 °C. (Found: Nd, 14.70%; C₃₇H₅₉I₂N₂NdO₄ (993.90) requires Nd, 14.51%). IR (Nujol): 1666 s, 1589 m, 1525 s, 1336 w, 1279 m, 1260 w, 1195 m, 1099 m, 1074 s, 1010 s, 945 w, 914 m, 854 s, 800 w, 755 s, 723 m, 668 m cm⁻¹. ¹H NMR (400 MHz, C₆D₆, ppm): δ = 31.19 ppm (1H; NC(H)N), 10.10 (4H; CH, Ar), 8.41 (2H; CH, Ar), 4.79 (8H; CH₂), 2.61 (4H; OCH₂, thf), 1.41 (4H; CH₂, thf), 1.11(12H; CH₃). Crystals dried before the spectrum was recorded hence loss of thf.

[Gd(EtForm)I₂(thf)₃] · thf 9

Colourless crystals (0.210 g, 83%), M.p. 177–179 °C. (Found: Gd, 15.83%; C₃₇H₅₉GdI₂N₂O₄ (1006.91) requires Gd, 15.62%); IR (Nujol): 1672 s, 1590 w, 1528 w, 1341 w, 1275 w, 1178 w, 1074 m, 1017 w,

915 w, 868 w, 800 m, 754w, 722 m cm⁻¹. IR suggests some loss of thf from the sample

[Tb(EtForm)I₂(thf)₃] · thf 10

Colourless crystals (0.207 g, 82%), M.p. 222–224 °C. (Found: Tb, 15.89%; C₃₇H₅₉I₂N₂O₄Tb (1008.58) requires Tb, 15.76%). IR (Nujol): 1664 m, 1593 m, 1528 s, 1342 w, 1275 s, 1239 w, 1198 m, 1103 m, 1073 s, 1012 s, 949 m, 915 m, 856 s, 797w, 775 m, 752 s, 724 w cm⁻¹.

[Dy(EtForm)I₂(thf)₃] · thf 11

Colourless crystals (0.184 g, 73%), M.p. 254–256 °C. (Found: Dy, 16.45%; C₃₇H₅₉DyI₂N₂O₄ (1012.16) requires Dy, 16.05%, loss of 0.5 thf of crystallisation, C₃₅H₅₅DyI₂N₂O_{3.5} (976.13) requires Dy, 16.65%). IR (Nujol): 1676 m, 1592 m, 1534 m, 1333 w, 1276 s, 1200s, 1104 m, 1070 m, 10122 s, 949 m, 915 s, 866 s, 802 m, 759 s, 734 m cm⁻¹.

[Ho(EtForm)I₂(thf)₃] · thf 12

Colorless crystals (0.193 g, 76%), M.p. 238–240 °C. (Found: Ho, 16.41%; C₃₇H₅₉HoI₂N₂O₄ (1014.59) requires Ho, 16.26%), IR (Nujol): 1663 m, 1592 s, 1530 s, 1334 w, 1274 s, 1199 m, 1104 s, 1074 s, 1012 m, 948 m, 914 m, 857 w, 800 m, 775 m, 755 m, 733 m, 666 s cm⁻¹. IR suggests some loss of thf from sample.

[Er(EtForm)I₂(thf)₃] · thf 13

Pink crystals (0.186 g, 73%), M.p. 156–158 °C. (Found: Er, 16.75%; C₃₇H₅₉ErI₂N₂O₄ (1016.92) requires Er, 16.45%). IR (Nujol): 1652 m, 1592 m, 1529 s, 1337 w, 1273 s, 1200s, 1104 m, 1073 m, 1012 s, 949 m, 915 s, 858 s, 801 m, 756 s, 722 m cm⁻¹.

[Lu(EtForm)I₂(thf)₃] · thf 14

Colourless crystals (0.203 g, 79%), M.p. 150–152 °C. (Found: Lu, 17.21%; C₃₇H₅₉LuI₂N₂O₄ (1024.63) requires Lu, 17.08%). IR (Nujol): 1666 m, 1593 m, 1535 s, 1342w, 1274 s, 1200 m, 1103 m, 1074 m, 1008 s, 948 w, 915 w, 894 w, 851 s, 799 w, 774 w, 755 m, 723 m, 666 m cm⁻¹. ¹H NMR (400 MHz, C₆D₆, ppm): δ = 8.05 ppm (1H; NC(H)N), 7.11 (4H; CH, Ar), 7.07 (2H; CH, Ar), 3.70 (16H; OCH₂, thf), 3.25 (8H; CH₂), 1.37 (12H; CH₃), 1.25 (16H; CH₂, thf).

[Ce(XylForm)I₂(thf)₃] · 1.5 thf 15

Yellow crystals (0.189 g, 78%), M.p. 232–234 °C. (Found: Ce, 16.18%; C₃₅H₅₅CeI₂N₂O_{4.5} (969.73) requires Ce 14.45%, loss of 1.5 thf of crystallisation, C₂₉H₄₃CeI₂N₂O₃ (861.59) requires Ce 16.26%). IR (Nujol): 1676 m, 1592 m, 1522 s, 1287 s, 1206 s, 1092 s, 1015 s, 942 m, 918 s, 858 s, 772 s, 723 w cm⁻¹. The solution was dried under vacuum, and the powder was used for ¹H NMR, ¹H NMR (400 MHz, C₆D₆, ppm): δ = 25.83 ppm (1H; NC(H)N), 8.16–7.66 (6H; CH, Ar), 2.37 (12H; CH₃).

[Nd(XylForm)I₂(thf)₃] · thf 16

Purple crystals (0.164 g, 70%), M.p. 202–204 °C. (Found: Nd, 17.02%; C₃₃H₅₁I₂N₂NdO₄ (937.79) requires Nd, 15.38%, loss of one thf of crystallisation, C₂₉H₄₃I₂N₂NdO₃ (865.71) requires Nd, 16.66%). IR (Nujol): 1675 m, 1592 m, 1521 s, 1282 s, 1205 s, 1071 s, 1018 s, 942 m, 915 s, 861 s, 772 s, 726 w cm⁻¹.

[Gd(XylForm)₂(thf)₃]-thf 17

Colourless crystals (0.200 g, 84%), M.p. 196–198 °C. (Found: Gd, 18.21%; C₃₃H₅₁GdI₂N₂O₄ (950.80) requires Gd, 16.54%, loss of one thf of crystallisation, C₂₉H₄₃GdI₂N₂O₃ (878.72) requires Gd, 17.90%). IR (Nujol): 1669 m, 1593 m, 1526 s, 1283 s, 1208 s, 1073 s, 1019 s, 945 m, 916 s, 859 s, 774 s, 725 w cm⁻¹.

[Tm(XylForm)₂(thf)₃]-thf 18

Colourless crystals (0.196 g, 81%), M.p. 162–164 °C. (Found: Tm, 18.24%; C₃₃H₅₁I₂N₂O₄Tm (962.48) requires Tm, 17.55%, loss of 0.5 thf of crystallisation, C₃₁H₄₇I₂N₂O_{3.5}Tm (926.46) requires Tm, 18.23%). IR (Nujol): 1670 m, 1593 m, 1528 s, 1281 s, 1209 s, 1071 s, 1018 s, 946 m, 915 s, 860s, 770s, 728 w cm⁻¹.

[Lu(XylForm)₂(thf)₃]-thf 19

Colourless crystals (0.172 g, 71%), M.p. 260–262 °C. (Found: Lu, 19.86%; C₃₃H₅₁I₂LuN₂O₄ (968.53) requires Lu, 18.07%, loss of one thf of crystallisation, C₂₉H₄₃I₂LuN₂O₃ (896.44) requires Lu, 19.52%). IR (Nujol): 1676 s, 1594 m, 1527 m, 1263 s, 1209 m, 1075 s, 1022 s, 956 m, 917 m, 866 m, 790s, 722 m cm⁻¹. ¹H NMR (400 MHz, C₆D₆, ppm): δ = 7.66 ppm (1H; NC(H)N), 6.95–7.03 (6H; CH, Ar), 3.77 (16H; OCH₂, thf), 2.71 (12H; CH₃), 1.25 (16H; CH₂, thf).

[Nd(PhForm)₂(thf)₃] 20

Purple crystals (0.138 g, 68%), M.p. 214–216 °C. (Found: Nd, 17.56%; C₂₅H₃₅I₂N₂NdO₃ (809.59) requires Nd, 17.82%). IR (Nujol): 1686 m, 1595 m, 1527 m, 1262 s, 1217 w, 1074 s, 1018 vs, 945 m, 918 m, 862 m, 802 vs, 756 m cm⁻¹.

[Gd(PhForm)₂(thf)₃] 21

Colourless crystals (0.168 g, 82%), M.p. 172–174 °C. (Found: Gd, 19.45%; C₂₅H₃₅GdI₂N₂O₃ (822.60) requires Gd, 19.12%). IR (Nujol): 1685 m, 1594 m, 1527 m, 1261 s, 1224 w, 1093 s, 1019 vs, 946 m, 917 m, 862 m, 800 vs, 758 m cm⁻¹.

[Er(PhForm)₂(thf)₃] 22

Pink crystals (0.162 g, 78%), M.p. 158–160 °C. (Found: Er, 19.87%; C₂₅H₃₅ErI₂N₂O₃ (832.61) requires Er, 20.09%). IR (Nujol): 1667 m, 1587 m, 1533 m, 1261 s, 1227 m, 1074 s, 1017vs, 947 m, 918 m, 854 m, 805 vs, 766 m cm⁻¹.

[Ce(XylForm)₂(thf)₂]-2.25 thf 23

Cerium metal powder (2.0 mmol), iodine (0.5 mmol), XylFormH (2.0 mmol) and dry THF (10 ml) were placed in a Schlenk flask in a nitrogen-filled dry box. The mixture was ultrasonicated for three days, and the reaction mixture was filtered. Yellow crystals (0.426 g, 79%), M.p. 180–182 °C. (Found: Ce, 15.78%; C₅₁H₇₂CeI₂N₄O_{4.25} (1076.14) requires Ce, 13.07%, loss of 2.25 thf of crystallisation, C₄₂H₅₄CeI₂N₄O₂ (913.92) requires Ce 15.33%). IR (Nujol): 1667 m, 1593 m, 1532 s, 1278 s, 1210s, 1193 m, 1094 m, 1074 s, 1012 s, 946 m, 916 m, 854 m, 771 m, 733 w cm⁻¹.

General procedure for 24–27

Lanthanoid metal powder (1.0 mmol), iodine (0.5 mmol), Dipp-FormH (1.0 mmol) and dry THF (10 ml) were placed in a Schlenk

flask in a nitrogen-filled dry box. The mixture was ultrasonicated for three days. The reaction mixture was filtered and crystals were obtained after the filtrate was evaporated to half volume under vacuum.

[Eu(DippForm)I(thf)₄]-thf 24

Green crystals (0.562 g, 56%), M.p. 270–272 °C. **7** crystallized in the monoclinic space group *P*₂₁/*c*, *a* = 16.359(3) Å, *b* = 16.776(3) Å, *c* = 17.082(3) Å, β = 91.64(3)°, *V* = 4686.0(16) Å³, which is similar to that reported,^[17] monoclinic space group *P*₂₁/*c*, *a* = 16.326(3) Å, *b* = 16.752(3) Å, *c* = 17.069(3) Å, β = 91.62(3)°, *V* = 4666.4(16) Å³. IR (Nujol): 1665 m, 1593 m, 1518 m, 1320 m, 1295 s, 1254 m, 1234 m, 1187 s, 1100 m, 1074 s, 1035 s, 993 m, 916 s, 884 s, 801 s, 756 s, 723 m cm⁻¹. The IR was consistent with the reported one.^[17]

[Yb(DippForm)I(thf)₃]-2DippFormH 25

Orange crystals (0.501 g, 62%), decompose 188 °C. IR (Nujol): 1669 s, 1589 m, 1525 s, 1338 w, 1317 w, 1289 s, 1261 s, 1237 w, 1188 m, 1098 m, 1075 s, 1030 vs, 952 w, 916 m, 874 s, 801 s, 757 s, 723 s cm⁻¹.

[Sm(DippForm)I(thf)₄]-thf 26 and [Sm(DippForm)I₂(thf)₃]-0.5 thf 27

26 blue crystals (M.p. 280 °C), Vis/NIR: Sm^{II} 424, 576, 624, Sm^{III} 921, 1207, 1381, 1717 nm, very sensitive to the air (colour change from blue to yellow within seconds), and [Sm(DippForm)I₂(thf)₃]-0.5thf **27** was obtained, yellow crystals (0.423 g, 83%), M.p. 238–240 °C. IR (Nujol): 1665 m, 1587 m, 1332 m, 1286 s, 1261 s, 1234 m, 1180s, 1097 s, 1020 s, 936 m, 800s, 753 m, 721 m cm⁻¹. Vis/NIR: 921, 1207, 1381, 1717 nm. **27** has some limited stability in air.

[Sm(XylForm)I(thf)₃]_n 28

Samarium metal powder (2.0 mmol), iodine (0.5 mmol), XylFormH (1.0 mmol) and dry THF (10 ml) were placed in a Schlenk flask in a nitrogen-filled dry box. The mixture was ultrasonicated for three days, and the reaction mixture was filtered. Blue crystals, M.p. 198 °C decomposed. IR (Nujol): 1648 m, 1588 m, 1560 m, 1342 m, 1297 m, 1260 m, 1201 m, 1179 m, 1074 m, 1030 vs, 953 w, 918 s, 870 vs, 758 m, 722 m cm⁻¹.

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Conflict of Interests

There are no conflicts of interest to declare.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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