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Stoichiometric Control: 8- and 10-coordinate $Ln(hfac)_3(bpy)$ and $Ln(hfac)_3(bpy)_2$ Complexes of the Early Lanthanides La – Sm†

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The coordination sphere of early lanthanide(III) ions is highly versatile, exhibiting the ability to form 8-, 9-, and 10-coordinate complexes with the same ligand set. The ability to isolate 10-coordinate complexes decreases across the period, and the late lanthanides typically cannot support a coordination number higher than eight. Using two common, commercially available ligands, hfac (1,1,1,5,5,5-hexafluoroacetylacetonato-) and bpy (2,2′-bipyridine), the 8- and 10- coordinate series $Ln(hfac)_3(bpy)$ and $Ln(hfac)_3(bpy)_2$ (Ln = La – Sm) are compiled in a single investigation, demonstrating that the desired coordination number can be targeted through stoichiometry. Solvent-free syntheses of $Ln(hfac)_3(bpy)$ and $Ln(hfac)_3(bpy)_2$ complexes from $Ln(hfac)_3(H_2O)_3$ precursors are investigated using a mechanochemical approach. Structural and spectroscopic properties as well as melting point trends are reported for the series.

Introduction

One of the major differences between the chemistry of lanthanides and that of transition metals is the nature of bonding. Unlike transition metals, wherein interaction between ligand orbitals and the metal frontier d-orbitals directs the coordination geometry and is responsible for many of the chemical and physical properties, bonding in lanthanides is primarily electrostatic. Owing to their radial distribution, the frontier 4*f* orbitals are essentially inaccessible for interaction with the ligand orbitals. The electrostatic nature of bonding in lanthanides provides an opportunity to synthesize lanthanide complexes of varying coordination number with the same ligand set, simply by altering the stoichiometry of the reaction. The early lanthanides are particularly well-suited to this endeavor owing to their large effective ionic radii which can readily accommodate coordination numbers from 8 to 10 for typical ligands.[1]

Early descriptions of the trend in lanthanide ionic radius assumed a monotonic decrease across the series.[2] In a more recent approach by Raymond et al.,[3] the change in lanthanide ionic radius is recognized as a quadratic decrease, and is most dramatic in the early lanthanides, from La through Sm. The variability in coordination number is nicely illustrated by the $Ln(hfac)_3(DME)_n$ series (DME = 1,2-dimethoxyethane). Therein, the 8-coordinate (n = 1) complexes are reported for Ln = La – Lu (excluding Pm),[4] but the 10-coordinate (n = 2) complex is actually preferred for La and a 9-coordinate complex in which one DME acts as a bridging ligand between two Ce centers is readily isolated.[5]

One of the drawbacks to the electrostatic bonding in lanthanide complexes is an apparent lack of control with respect to the resulting structure. It is commonly assumed that the ionic radius is the primary dictator of coordination number as opposed to stoichiometric availability of ligands. However, we demonstrate that by using the appropriate experimental conditions, the coordination number and product expected from stoichiometry is obtained reliably.

In general, lanthanides have high hydration enthalpies, and for the early lanthanides in particular (e.g., La and Ce), coordination of water molecules to increase the coordination number above 8 is not uncommon. Equally, for mid-size Ln(III) ions Nd and Sm, water can displace a bidentate ligand to lower the coordination number below 10. We demonstrate that, with adequate care, hydration can be avoided and both 8- and 10-coordinate complexes can be obtained with the same ligand set for Ln = La, Ce, Pr, Nd, and Sm. It is worth noting that fully characterized series of 10-coordinate complexes are currently not common in the literature. Understanding how to manipulate the coordination environment, selecting either an 8- or a 10-coordinate complex, is

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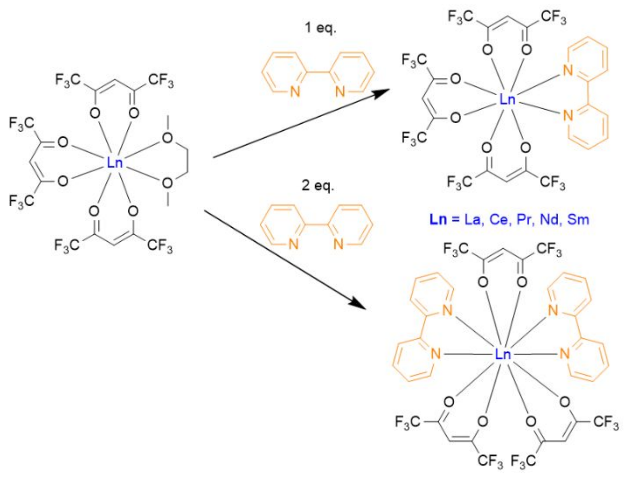
†Electronic Supplementary Information (ESI) available: crystallographic details and CIF files for $Ln(hfac)_3(bpy)$ (Ln = La, Ce, Pr, Nd, Sm and $Ln(hfac)_3(bpy)_2$ (Ln = Ce, Pr, Nd, Sm); IR, DSC and PXRD characterization of mechanochemical reactions; see DOI: 10.1039/x0xx00000x

relevant to the development of these and other similar monomeric, volatile, low-melting point solids, which have potential applications as CVD precursors.[6]

Mechanochemical synthesis[7,8] is gaining attention as an alternative to standard solution-based techniques. Using only a few drops of solvent for liquid-assisted grinding (LAG),[7,9] or omitting the solvent altogether, mechanochemical synthesis is considered "greener", and there is mounting evidence that atypical products and solid phases can be obtained mechanochemically.[10] The progress of solid-state reactions can be monitored readily using FTIR or PXRD, either in situ or by sampling aliquots at regular intervals.[11] Whereas examples of mechanochemical synthesis of transition metal complexes,[12] metal-organic frameworks,[13] and nanoparticles[14] are increasingly common, there are few examples of lanthanide complexes prepared in this manner.[15] We compare standard solution techniques to the use of only a mortar and pestle as a means of preparing a range of simple lanthanide complexes.

Herein, we report our solution syntheses, and results of mechanochemical trials, for the isomorphous $Ln(hfac)_3(bpy)_2$ series of 10-coordinate complexes and the isomorphous $Ln(hfac)_3(bpy)$ series of 8-coordinate complexes; Ln = La, Ce, Pr, Nd, Sm (Scheme 1). We have selected common and commercially available ligands for this study, providing benchmark data for comparison with specialized ligands. β-Diketonates, particularly hfac, are popular ligands in the Ln(III) literature, often selected to increase solubility and provide charge balance for coordination complexes incorporating novel ligands.[6] 2,2′-Bipyridine (bpy) is a common ligand that provides a N,N-bidentate coordination, similar in bite-angle to numerous other ligands. Using $Ln(hfac)_3(H_2O)_3$ as the starting material, we demonstrate that the progress of the mechanochemical reaction, displacing H_2O with bpy, can be determined by the disappearance in the IR spectrum of the OH vibrational band at ~3400 cm^{-1} (Figure S1).† Furthermore, 8-, 9-, and 10-coordinate complexes can be distinguished by absorptions at 800, 796, and 792 cm^{-1} respectively (Figure S1).† We report melting point trends for the series and provide structural data for those species not previously reported. Finally, we compare anhydrous complexes to the ostensibly 9-coordinate $Ln(hfac)_3(bpy)(H_2O)$ hydrates.



Scheme 1. Synthetic scheme for the preparation of anhydrous Ln(hfac)3(bpy) and Ln(hfac)3(bpy)2

Results and Discussion

$La(hfac)_3(bpy)_2$ was first reported by Reedijk *et al.* in 2001.[16] In that work, electron withdrawing groups, such as hfac, were explored as a means to stabilize 10-coordinate lanthanide complexes of Ln(III) ions smaller than La, and the synthesis of $Sm(hfac)_3(bpy)_2$ was claimed. Only the structure of the La complex was reported however, as well as the structure of the hydrate $[Sm(hfac)_3(bpy)(H_2O)]\cdot(bpy)$, which is actually a 9-coordinate complex co-crystallized with an uncoordinated 2,2′-bipyridine molecule in a 1:1 ratio. In 2009, Kawai *et al*. reported the deep red emission band of a complex claimed to be $Sm(hfac)_3(bpy)_2$,[17] however they did not report characterization data that unequivocally identifies their analyte as the anhydrous 10-coordinate species as opposed to the 9-coordinate hydrate observed by Reedijk. In 2015, Ahmed and Iftikar reported the structure of the 9-coordinate neodymium hydrate $[Nd(hfac)_3(bpy)(H_2O)]\cdot 0.5(bpy)$.[18] Although similar in structure to the samarium hydrate, the co-crystallization with 2,2′-bipyridine occurs in a different ratio, 2:1 for Nd compared to 1:1 in for the Sm complex.

In our synthetic experience with the $Ln(hfac)_3(bpy)_2$ series, we have observed that the smaller Nd(III) and Sm(III) ions have a larger propensity for the formation of the 9-coordinate hydrate compared to the larger La(III) – Pr(III) ions. Even when starting with the anhydrous precursor $Ln(hfac)_3(DME)$, care must be taken to avoid formation of the hydrate; DME = 1,2-dimethoxyethane. Indeed, the 10-coordinate $Ln(hfac)_3(bpy)_2$ complexes of the smaller Nd and Sm ions can decompose to form 9-coordinate hydrates, losing a bpy ligand and picking up a water ligand, when handled in the presence of atmospheric moisture. Interestingly, the trend in increased moisture-sensitivity with decreasing lanthanide ion radius for these 10-coordinate species contrasts with the behaviour of our precursor 8-coordinate $Ln(hfac)_3(DME)$ complexes. In the latter, complexes of the lighter, larger lanthanides exhibit higher moisture-sensitivity. The 8-coordinate La, Ce and, to a lesser extent Pr, complexes exhibit a propensity to pick up water from the atmosphere to form 9-coordinate hydrate species.[4,19]

Here, we complete the $Ln(hfac)_3(bpy)_2$ structural series for La through Sm, omitting Pm (Figure 1; Table 1), and compare and contrast the analogous 8-coordinate complexes (Table 2). As with other Ln(III) coordination series, the melting point can be a quick, reliable and inexpensive method of identifying the complex. The melting points of the species discussed herein are tabulated for quick future reference in Table 3.

Structure and Melting Point Trends

A single crystallographic form is observed for the series of 10-coordinate Ln(hfac)$_3$(bpy)$_2$ complexes, from La(III) to Sm(III), excluding Pm(III). The structures are essentially isomorphous across the series. Interestingly, the structure solutions present an unusual case in which it is unclear whether they are best solved in *Cc* or in *C*2/*c*. These two crystal systems differ only in the absence or presence of a glide plane and cannot be differentiated based on systematic absences. Since *Cc* is non-centrosymmetric and *C*2/*c* is centrosymmetric, E-statistics might be used (cautiously) as an additional guide to selecting the space group because centrosymmetric crystals tend to have a larger number of weak Bragg reflections. In the present case, however, the data are too weak to employ E-statistics in a meaningful way. We have selected *C*2/*c* as the space group that generates the slightly better solution (lower R values), and which maintains consistency with the literature structure for La.[16]

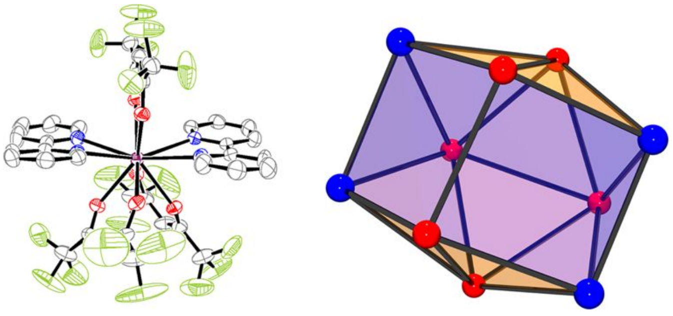


Figure 1. (Left) ORTEP representation of Sm(hfac)$_3$(bpy)$_2$ is representative of the series; thermal ellipsoids rendered at 50%; (Right) positions of the coordinating N atoms (blue) and O atoms (red) about a central Ln(III) ion (not shown) describe a sphenocorona (quadrilaterals in purple).

Table 1. Crystallographic data for Ln(hfac)$_3$(bpy)$_2$ complexes

	La(hfac)$_3$(bpy)$_2$^{a}	**Ce(hfac)$_3$(bpy)$_2$**	**Pr(hfac)$_3$(bpy)$_2$**	**Nd(hfac)$_3$(bpy)$_2$**	**Sm(hfac)$_3$(bpy)$_2$**
Formula	$LaC_{35}H_{19}F_{18}N_4O_6$	$CeC_{35}H_{19}F_{18}N_4O_6$	$PrC_{35}H_{19}F_{18}N_4O_6$	$NdC_{35}H_{19}F_{18}N_4O_6$	$SmC_{35}H_{19}F_{18}N_4O_6$
F.W.	1072.45	1073.66	1074.45	1077.78	1083.89
T (K)	213	150(2)	150(2)	150(2)	150(2)
Crystal color	colorless	orange	green	purple	colorless
Crystal habit	parallelepiped	block	block	prism	block
Crystal size (mm)	0.54 × 0.50 × 0.40	0.45 × 0.32 × 0.30	0.24 × 0.14 × 0.14	0.4 × 0.3 × 0.2	0.32 × 0.30 × 0.14
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space Group	*C*2/*c*	*C*2/*c*	*C*2/*c*	*C*2/*c*	*C*2/*c*
a (Å)	21.928(2)	21.819(4)	21.786(4)	21.7670(2)	21.775(4)
b (Å)	11.9096(12)	11.828(2)	11.792(2)	11.76298(8)	11.724(2)
c (Å)	18.183(2)	18.116(4)	18.081(4)	18.04081(18)	18.017(4)
β (°)	118.99(2)	118.98(3)	118.89(3)	118.8228(13)	118.73(3)
V (Å^3)	4153.6(7)	4089.8(18)	4066.8(18)	4046.99(8)	4033.4(18)
Z	4	4	4	4	4
Reflections collected/ unique (R_{int})	19698 / 6016 (0.0231)	20796 / 3613 (0.0808)	16383 / 3594 (0.0631)	55896 / 7201 (0.0248)	23131 / 3564 (0.0561)
μ (mm^{-1})	-	1.244	1.329	1.415	1.588
data/ restraints/ parameters	6003 / 60 / 346	3613 / 121 / 318	3594 / 147 / 375	7201 / 500 / 374	3564 / 147 / 375
GOF	1.040	1.067	1.049	1.104	1.069
$R_1(I>2\sigma)$	0.0479	0.0556	0.0457	0.0449	0.0348
w$R_2(I>2\sigma)$	0.0479	0.1282	0.0971	0.1305	0.0759
R_1 (all data)	-	0.0763	0.0620	0.0479	0.0411
wR_2 (all data)	0.137	0.1453	0.1076	0.1348	0.0798
CCDC deposition	EBUXUU	1856929	1858639^b	1856933	1856932

^{a} Data from literature: CSD refcode EBUXUU.[16]

^{b} Pr(hfac)$_3$(bpy)$_2$ was previously obtained, however, its unit cell is sufficiently different from that reported in Table 1: CSD refcode XOYRAG.[20]

Table 2. Crystallographic data for Ln(hfac)$_3$(bpy) complexes

	La(hfac)$_3$(bpy)	**Ce(hfac)$_3$(bpy)**	**Pr(hfac)$_3$(bpy)**	**Nd(hfac)$_3$(bpy)**	**Sm(hfac)$_3$(bpy)**
Formula	$LaC_{25}H_{11}F_{18}N_2O_6$	$CeC_{25}H_{11}F_{18}N_2O_6$	$PrC_{25}H_{11}F_{18}N_2O_6$	$NdC_{25}H_{11}F_{18}N_2O_6$	$SmC_{25}H_{11}F_{18}N_2O_6$
F.W.	916.27	917.48	918.27	921.60	927.71
T (K)	150(2)	150(2)	150(2)	150(2)	150(2)
Crystal color	colorless	orange	green	Purple	colorless
Crystal habit	block	block	block	block	plate
Crystal size (mm)	0.26 × 0.22 × 0.12	0.18 × 0.14 × 0.08	0.18 × 0.12 × 0.10	0.6 × 0.5 × 0.2	0.24 × 0.20 × 0.05
Crystal system	triclinic	triclinic	triclinic	triclinic	triclinic
Space Group	*P*-1	*P*-1	*P*-1	*P*-1	*P*-1
a (Å)	12.040(2)	11.993(2)	11.9492(3)	11.9200(3)	11.8612(19)
b (Å)	15.830(3)	15.829(3)	15.8540(5)	15.8414(3)	15.851(3)
c (Å)	17.855(4)	17.833(4)	17.8253(5)	17.8065(4)	17.880(3)
α (°)	78.40(3)	78.46(3)	78.5449(14)	78.642(2)	78.721(3)
β (°)	76.30(3)	76.46(3)	76.6137(16)	76.711(2)	76.813(4)
γ (°)	72.70(3)	72.69(3)	72.7269(15)	72.859(2)	72.850(3)
V (Å^3)	3125.3(11)	3111.0(11)	3106.17(15)	3096.69(12)	3097.6(8)
Z	4	4	4	4	4
Reflections collected/ unique (R_{int})	33367/ 11029 (0.0609)	27831 / 10940 (0.0856)	33787 / 10948 (0.0671)	49263 / 10914 (0.0379)	30731 / 10844 (0.0915)
μ (mm^{-1})	1.517	1.614	1.720	1.828	2.047
data/ restraints/ parameters	11029/ 351/ 961	10940 / 30/ 961	10948 / 348 / 931	10914 / 336 / 937	10844 / 297 / 922
GOF	1.060	1.055	1.037	1.063	1.021
R_1(I>2σ)	0.0611	0.0678	0.0555	0.0615	0.0664
wR_2(I>2σ)	0.1431	0.1652	0.1317	0.1614	0.1435
R_1 (all data)	0.0898	0.1412	0.0911	0.0626	0.1246
wR_2 (all data)	0.1618	0.2125	0.1564	0.1622	0.1696
CCDC deposition	1856921	1856922	1856925	1856926	1856928

Table 3. Visual melting points of pure materials

Ln(hfac)$_3$(bpy)$_2$						Hydrates[b]		
Ln	La	Ce	Pr	Nd[a]	Sm[a]		[Nd(hfac)$_3$(bpy)(H$_2$O)]·0.5(bpy)	[Sm(hfac)$_3$(bpy)(H$_2$O)]·(bpy)
m.p. (°C)	198-200	186-188	174-176	168-169	119-122	m.p. (°C)	175	173
Ln(hfac)$_3$(bpy)								
	La[a]	Ce[a]	Pr[a]	Nd[a]	Sm			
	127-130	126-128	136-138	140-141	139-141			

[a] inert atmosphere

[b] from Ahmed and Iftikhar[18]

In the crystalline solid, the molecular structure of the 10-coordinate Ln(hfac)$_3$(bpy)$_2$ exhibits a coordination geometry best described as a sphenocorona (Figure 1), one of the Johnson solids whose faces are composed of twelve equilateral triangles and two squares. The sphenocorona is typical of 10-coordinate lanthanide and actinide complexes, despite rarely being identified as such in the literature.[21] In the present species, the two N atoms of a single bpy ligand and the two O atoms of a single hfac ligand describe the quadrilateral faces of the polyhedron.

With no short intermolecular contacts and no obvious supramolecular synthons, the crystal packing of Ln(hfac)$_3$(bpy)$_2$ appears to be directed primarily by the efficiency with which the molecular shapes can be organized and interlocked. A convenient representation is to view the structures as linear arrays of molecules propagating in [001] (Figure 2). The bpy ligands of neighbouring molecules are then arranged in an offset π-stack, with interplanar distances slightly greater than ~3.4 Å, typical for planar closed-shell hydrocarbons.[22]

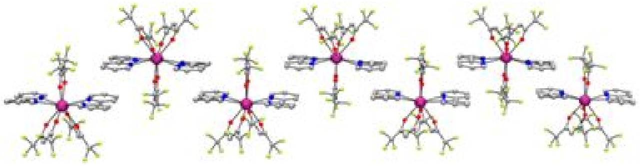


Figure 2. Crystal packing of Sm(hfac)$_3$(bpy)$_2$ illustrating the chain-like arrangements propagating in [001].

Interestingly, the unit cell parameters, coordination environment, and packing motif of La(hfac)$_3$(bpy)$_2$ bear a strong resemblance to those of the *C*2/*c* phases of La(hfac)$_3$(pyDTDA)$_2$,[23] a material incorporating pyDTDA neutral radical ligands[24] and exhibiting re-entrant phase behaviour; pyDTDA = 4-(2′-pyridyl)-1,2,3,5-dithiadiazolyl. The structural similarities make the Ln(hfac)$_3$(bpy)$_2$ series particularly useful as a model for the pyDTDA complexes and other complexes of specially designed bidentate ligands.

The crystal structures of the 8-coordinate complexes are isostructural and crystallize in the space group *P*–1 with two molecules in the asymmetric unit. The 8-coordinate complexes trend towards shorter Ln–N bond lengths with decreasing lanthanide size (Table S1),† indicating stronger bonding based on lanthanide and ligand interactions characterized primarily by electrostatics.[3,25] For the 10-coordinate complexes, the same trend is observed (Table S3).† In terms of their geometries, the 8-coordinate complexes could be described as distorted square anti-prism.[26] Using Haight's method, the Ln(hfac)$_3$(bpy) complexes become increasingly more square anti-prismatic (Table S2)† as the Ln^{3+} ion becomes smaller (La - Sm). Using an updated Shape Measures Parameter script, similar to one previously published,[27] we quantified the 8-coordinate complexes are closer to square anti-prism (D_{4d}) compared to dodecahedron (D_{2d}), in agreement with Haight's method for assigning coordination geometries to 8-coordinate structures.

The visual melting points of the Ln(hfac)$_3$(bpy)$_2$ species were recorded across the series. Measurements were performed in air, with the exception of Ln = Nd, Sm, both of which readily form the hydrate in air. A roughly linear decrease in melting point is observed from La through Nd, but the melting point of Ln = Sm is significantly lower than the trend predicts and is closer to the melting point of 2,2′-bipyridine (70 - 73 °C) suggesting dissociation of bpy prior to melting in the case of the Sm complex. The visual melting points of the 8-coordinate Ln(hfac)$_3$(bpy) are lower than those of the 10-coordinate Ln(hfac)$_3$(bpy)$_2$, with the exception of Ln = Sm.

Solution Synthesis

The 8-coordinate Ln(hfac)$_3$(bpy) complexes of the larger lanthanides (Ln = La, Ce, Pr, and Nd) are air-sensitive. Careful handling of these lanthanide complexes is required owing to their propensity to form 9-coordinate Ln(hfac)$_3$(bpy)(H$_2$O) hydrates upon exposure to solvent-borne or atmospheric moisture. Nevertheless, successful synthesis of the anhydrous 8-coordinate complexes can be achieved in air if an anhydrous precursor is used in a non-polar solvent. We employed Ln(hfac)$_3$(DME) and hexanes. Once the solid products were recovered, they were immediately transferred to an argon-filled glovebox for storage to avoid decomposition via hydration. Only the Sm 8-coordinate complex could be stored indefinitely in air. All 8-coordinate complexes were sublimed to obtain material of sufficiently high purity for melting point analysis (Table 3) and single crystals for structural analysis where needed.

The 10-coordinate Ln(hfac)$_3$(bpy)$_2$ complexes of smaller lanthanide ions, Nd and Sm, are air-sensitive owing to a propensity to form a 9-coordinate hydrate wherein one bpy ligand is displaced from the inner coordination sphere to the outer sphere. The crystalline phase of this decomposition is an inclusion complex with bpy. In the case of Nd, synthesis of the air-sensitive 10-coordinate complexes was achieved in air using Ln(hfac)$_3$(DME) and hexanes, and the solid product was stored under inert atmosphere. For Sm, however, solution synthesis of the 10-coordinate complexes was only successful using anhydrous hexane under inert atmosphere and could not be replicated in air. To achieve high product purity adequate for melting point characterization, 10-coordinate complexes were recrystallized from a mixture of 1:1 hexanes and methylene chloride.

Mechanochemical Synthesis

Mechanochemical syntheses of Ln(hfac)$_3$(bpy) and Ln(hfac)$_3$(bpy)$_2$ were explored using Ln(hfac)$_3$(H$_2$O)$_3$ hydrates as starting materials. Omitting solvent and using the hydrate precursor rather than the DME precursor simplifies these reactions and makes them "greener". All product characterization is reported on the crude material, without further purification by solution crystallization or sublimation. Not surprisingly, the melting points of these crude products are *ca*. 10 °C lower and exhibit larger melting ranges than the pure materials reported in Table 3. The coordination number of the lanthanide complexes was identified by probing the 800 cm^{-1} region of the IR spectrum (see ESI).† The ν(C-H) vibrational bend shifts to lower energy with increasing coordination number, going from 800 cm^{-1} (observed as a shoulder in a broader peak at 803 cm^{-1}) for the 8-coordinate complexes, to a clearly identifiable peak at 796 cm^{-1} for 9-coordinate, and 792 cm^{-1} for 10-coordinate complexes. The 3400 cm^{-1} region of the IR spectrum, wherein ν(O-H) for H$_2$O is clearly evident, was also used to probe reaction progress and identify the formation of anhydrous species. PXRD patterns of products were used to corroborate the findings of the IR analysis.

Of the 8-coordinate lanthanide complexes described herein, Sm(hfac)$_3$(bpy) is the only one stable in air. Thus, we undertook the mechanochemical synthesis of the 8-coordinate Sm complex first. Grinding one equivalent of bpy with Sm(hfac)$_3$(H$_2$O)$_2$ in air, we observed complete conversion to the anhydrous 8-coordinate Sm(hfac)$_3$(bpy) complex within ~20 minutes. For Pr(hfac)$_3$(H$_2$O)$_3$ and Nd(hfac)$_3$(H$_2$O)$_3$, when ground with 1 equivalent of bpy in air, IR spectra indicate that hydrated 9-coordinate complexes are afforded, confirming stoichiometric coordination of one bpy ligand as well as stability of the 9-coordinate hydrates in air. For the largest lanthanides (La and Ce), using 1 equivalent of bpy in air results in product mixtures of the 10-coordinate complex and a hydrated 9-coordinate complex. Repeating the trial with La under dry Ar$_{(g)}$ atmosphere does not alter the results. The observation of 10-coordinate complex suggests that, in contrast to the solvent-based approach, mechanochemical synthesis does not impart stoichiometric control for the La and Ce species. For the larger lanthanides, the 8-coordinate complexes are only accessible via solution synthesis.

Mechanochemical reaction of two equivalents of 2,2'-bipyridine with Ln(hfac)$_3$(H$_2$O)$_3$ (Ln = La, Ce, and Pr) in air affords the Ln(hfac)$_3$(bpy)$_2$ complexes, as expected. Surprisingly, there is evidence that the 10-coordinate complex of Nd is also accessible in this manner, although it appears to be combined with the 9-coordinate hydrate. Standard solution synthesis of anhydrous Sm(hfac)$_3$(bpy)$_2$ is challenging on account of the propensity to form the 9-coordinate Sm(hfac)$_3$(bpy)(H$_2$O)·(bpy). We investigated the mechanochemical synthesis in air as a potential alternate route to the anhydrous 10-coordinate Sm(hfac)$_3$(bpy)$_2$ complex. Complicating the analysis, the ν(O-H) associated with H$_2$O in the IR spectrum of [Sm(hfac)$_3$(bpy)(H$_2$O)]·(bpy) occurs at lower energy (~3200 cm^{-1}) and is weaker, compared to the other early 9-coordinate lanthanide hydrate complexes (ν(OH) ~3400 cm^{-1}). Grinding Sm(hfac)$_3$(H$_2$O)$_2$ with 2 equivalents of bpy in air appears to initially generate an anhydrous complex based on the absence of ν(O-H) in the IR spectrum. However, no peak at ~792 cm^{-1} associated with the 10-coordinate Sm(hfac)$_3$(bpy)$_2$ complex is seen and only a peak at 795 cm^{-1} associated with a 9-coordinate complex is observed. The product is hygroscopic and over time the IR spectrum begins to resemble that of [Sm(hfac)$_3$(bpy)(H$_2$O)]·(bpy). PXRD of the product corroborates the transformation into [Sm(hfac)$_3$(bpy)(H$_2$O)]·(bpy) quickly upon exposure to air.

Given the air-sensitivity of Sm(hfac)$_3$(bpy)$_2$ and the initially promising observations upon grinding the Sm(hfac)$_3$(H$_2$O)$_2$ precursor with two equivalents of bpy in air, we reproduced the synthetic attempt in a glovebox under dry Ar$_{(g)}$ atmosphere. After grinding for 20 minutes, an IR peak at 792 cm^{-1} is clearly apparent (see Supp. Info.), indicating the formation of a 10-coordinate species. A peak at 796 cm^{-1} is also present, indicating co-existence with the 9-coordinate hydrate. Interestingly, the ratio of 796 to 792 cm^{-1} is skewed in favor of the 10-coordinate complex when the product has been ground with KBr and pressed as a pellet, as compared to product prepared for IR analysis as a Nujol mull. As KBr is hygroscopic, grinding with KBr under inert atmosphere may indeed alter the product ratio in favor of the anhydrous Sm(hfac)$_3$(bpy)$_2$ complex. The ground reaction mixtures were allowed to age in the glovebox, both as a two-component mixture and as ground with KBr (three-component mixture). After 5 days, the ratio of 796 to 792 cm^{-1} remained unaltered, indicating that aging does not further the reaction, nor does it lead to decomposition.

Displacement of the *O,O*-bidentate ligand DME by *N,N*-bidentate bpy might be considered surprising on account of the generally accepted propensity of lanthanides to prefer harder O donors to N donors. Furthermore, the bond lengths for the 8-coordinate Ln-O$_{DME}$ are shorter than the comparable Ln-N$_{bpy}$ bonds (Table S4).† We speculate that the entire reaction environment must be taken into account to properly understand what is happening. DME is both more soluble and more volatile than bpy. Thus, in the solution-based reactions, the solvation enthalpy of DME *vs.* bpy may be a significant factor driving the reaction. In the mechanochemical synthesis, evaporation of displaced H$_2$O, which has a greater ΔH°_{vap} (44.0 kJ/mol) than even DME[28] (36.8 ± 0.2 kJ/mol) is likely a significant factor driving the reaction as 2,2′-bipyridine has ΔH°$_{sub}$ (70 - 83 kJ/mol)[29], and is indeed part of the design of these syntheses.

Experimental Section

Synthesis

Lanthanide precursors $LnCl_3(H_2O)_n$ were purchased from Strem, Alfa Aesar, Acros or Sigma Aldrich (Ln = La, Ce, Pr, Nd, Sm). $Ln(hfac)_3(H_2O)_n$ (n = 2, 3) starting materials were prepared from their $LnCl_3$ salts using a modified literature method.[30] 1,1,1,5,5,5-Hexafluoro-2,4-pentanedione (Hhfac), 1,2-dimethoxyethane (DME) and 2,2′-bipyridine (bpy) were purchased from Alfa Aesar, Acros and Alfa Aesar/Sigma Aldrich respectively. All reagents were used as received. Dried, degassed hexane and toluene were dispensed from an LC Solvent Purification System (SPS) using dry packed columns containing 3 Å molecular sieves and solvent kegs filled off-site by the manufacturer. Anhydrous $Ln(hfac)_3(DME)$ starting materials were prepared following literature methods.[4,5,31] Sublimations were carried out on a multistage programmable temperature tube furnace under a temperature gradient and reduced atmosphere. Temperature settings for the hottest zone, where the crude sample was loaded, are reported. Melting points were obtained using a Mel-Temp melting point apparatus. For species prepared at Guelph, IR spectra of pressed KBr pellets or Nujol mulls on NaCl plates were collected using a Nicolet 4700 FTIR spectrometer at ambient temperature; resolution 4 cm^{-1}.

Mechanochemical syntheses were performed at Louisiana Tech University by manual grinding employing an agate mortar and pestle in air, and using the $Ln(hfac)_3(H_2O)_n$ (Ln = La, Ce, Pr, Nd, Sm) hydrates as starting materials. IR spectra of Nujol mulls on KBr plates were collected at ambient temperature using a Mattson Genesis II FTIR spectrometer; resolution 1 cm^{-1}. Melting points were obtained using a Mel-Temp melting point apparatus. DSC was obtained using a TA Instruments Q2000 series calorimeter under N_2 atmosphere, step sizes were varied and are listed in the SI. PXRD patterns were obtained at Indiana University Bloomington using a Panalytical Empyrean instrument equipped with CuK$_\alpha$ radiation and X'Celerator linear strip detector. Simulated PXRD data were calculated using Mercury software[32] with a wavelength of 1.54056 Å.

$La(hfac)_3(bpy)$. 2,2′-Bipyridine (0.0950 g, 0.6082 mmol) was added to a solution of $La(hfac)_3(DME)$ (0.5145 g, 0.6052 mmol) in hexanes (100 mL) at room temperature with vigorous stirring. The colourless solution was stirred for 4 h, then decanted off a very small amount of white powdery material and concentrated to a white solid, using a rotary evaporator and minimal heating. The material was immediately transferred to a glovebox under $Ar_{(g)}$ atmosphere. The crude yield was quantitative. The white solid was sublimed at 115 °C (10^{-2} Torr) to generate colourless crystals; yield 0.3821 g (69%). M.p. (inert atmosphere) 127 - 130 °C. Anal. Calcd. for $LaC_{25}H_{11}N_2O_6F_{18}$: C, 32.77; H, 1.21; N, 3.06%. Found: C, 33.09; H, 1.46; N, 3.27%. IR (KBr) ν/cm^{-1}: 3305(vw), 3138(vw), 1654(s, br), 1601(m), 1579(m), 1560(m), 1532(ms), 1510(ms, br), 1492(ms), 1478(ms), 1439(ms), 1348(w), 1321(m), 1260(s), 1203(s), 1144(s), 1097(ms), 1064(mw), 1045(w), 1012(mw, sh), 1008(mw), 971(vw), 949(vw), 803(ms), 794(m, sh), 762(ms), 755(ms), 739(ms), 660(s), 646(mw), 626(w), 621(w), 582(ms), 527(mw), 461(w), 417(w, sh), 409(w). ^1H NMR (400 MHz, $CDCl_3$): δ(^1H) = 9.06 (d, 2H, J = 4.34 Hz), 8.00 (m, 2H), 7.52 (m, 4H), 5.98 (s, 3H, hfac). ^{13}C NMR (100 MHz, $CDCl_3$): δ(^{13}C) = 176.90 (q, $^2J_{C-F}$ = 34.70), 153.84, 150.28, 139.44, 125.11, 121.40, 117.45 (q, $^1J_{C-F}$ = 287.80), 90.91.

$Ce(hfac)_3(bpy)$. 2,2′-Bipyridine (0.0892 g, 0.548 mmol) was added to a solution of $Ce(hfac)_3(DME)$ (0.4664 g, 0.5478 mmol) in hexanes (100 mL) at room temperature with vigorous stirring. The pale yellow solution was stirred at room temperature for 2 h. The solution was concentrated to a pale yellow residue using a rotary evaporator and minimal heating. The solid residue was immediately transferred to a glovebox under Ar atmosphere. The crude yield was quantitative. The material was sublimed at 115 °C (10^{-1} Torr) to generate yellow crystals; yield 0.2589 g (52%). M.p. (inert atmosphere) 126 - 128 °C. Anal. Calcd. for $CeC_{25}H_{11}N_2O_6F_{18}$: C, 32.73; H, 1.21; N, 3.05%. Found: C, 32.57; H, 1.36; N, 3.17%. IR (KBr) ν/cm^{-1}: 3134(vw), 1661(ms), 1646(s), 1604(m), 1597(mw, sh), 1578(mw), 1560(m), 1533(m), 1491(ms), 1477(ms), 1457(m), 1441(mw), 1349(w), 1321(mw), 1255(s), 1207(s), 1144(s), 1098(ms), 1064(w), 1044(w), 1014(mw), 1005(w), 972(vw), 949(vw), 803(ms), 763(ms), 740(ms), 660(s), 646(mw), 627(w), 583(ms), 527(w), 462(w), 410(w).

$Pr(hfac)_3(bpy)$. 2,2′-Bipyridine (0.0900 g, 0.576 mmol) was added to a solution of $Pr(hfac)_3(DME)$ (0.4696 g, 0.5511 mmol) in hexanes (50 mL) at room temperature with vigorous stirring. The pale green solution was stirred for 1 h, and was then concentrated to a green solid, using a rotary evaporator and minimal heating. The solid was recrystallized from hexanes overnight at room temperature. The pale green crystals were recovered and immediately transferred to a glovebox under Ar atmosphere; yield 0.3641 g (72%). A 0.3236 g aliquot was sublimed at 115 °C (10^{-1} Torr) to generate pale green blocks suitable for X-ray analysis; yield 0.3093 g (69% as calculated from crude). M.p. (inert atmosphere) 136 - 138 °C. Anal. Calcd. for $PrC_{25}H_{11}N_2O_6F_{18}$: C, 32.70; H, 1.21; N, 3.05%. Found: C, 32.80; H, 1.05; N, 3.08%. IR (Nujol, NaCl) ν/cm^{-1}: 3133(vw), 1663(ms), 1646(s), 1604(m), 1578(mw), 1560(m), 1533(m), 1493(ms), 1477(ms), 1461(m), 1442(m), 1349(w), 1321(mw), 1256(s), 1206(s), 1145(s), 1099(ms), 1064(w), 1045(w), 1014(mw), 1007(w), 973(vw), 949(vw), 802(ms), 762(ms), 739(m), 660(s), 646(mw), 627(w), 584(ms), 527(w).

$Nd(hfac)_3(bpy)$. 2,2′-Bipyridine (0.1675 g, 1.072 mmol) was added to a solution of $Nd(hfac)_3(DME)$ (0.8955 g, 1.047 mmol) in hexanes (50 mL) at room temperature with vigorous stirring. The pale blue solution was stirred at room temperature for 4 h, then was concentrated to a blue-purple solid using a rotary evaporator and minimal heating. The solid was immediately introduced into a glovebox under dry argon atmosphere; yield 0.8670 g (90%). Purple crystals were prepared by sublimation at 110 °C (10^{-2} Torr); yield 0.3244 g (34%). M.p. (inert atmosphere) 140 - 141 °C. IR (Nujol, NaCl) ν/cm^{-1}: 3136 (vw), 1664 (m), 1645 (s), 1605 (m), 1578 (w), 1561 (m), 1533 (m), 1494 (s), 1463 (s), 1442 (w), 1377 (m), 1350 (w), 1321 (w), 1256 (s), 1206 (s), 1144 (s), 1099 (m), 1065 (vw), 1045 (vw), 1015 (w), 1007 (w), 973 (vw), 949 (vw), 891 (vw), 802 (s), 763 (s), 739 (m), 723 (vw), 660 (s), 646 (vw), 627 (vw), 583 (w). Anal. Calcd. for $NdC_{25}H_{11}N_2O_6F_{18}$: C, 32.58; H, 1.20; N, 3.04%; Found: C, 32.39; H, 1.39; N, 3.03%.

Sm(hfac)$_3$(bpy): solution synthesis. Excess 2,2′-bipyridine (0.1532 g, 0.9809 mmol) was added to a solution of Sm(hfac)$_3$(DME) (0.7768 g, 0.9015 mmol) in methylene chloride (45 mL) at room temperature with vigorous stirring. The colorless solution was stirred at room temperature for 1h, then was concentrated to a white solid, using a rotary evaporator and minimal heating. The solid was sublimed at 115 °C (10^{-2} Torr) to generate colorless plates; yield 0.7542 g (90%). M.p. (in air, 760 mm Hg) 139 - 141 °C. Anal. Calcd. for $SmC_{25}H_{11}N_2O_6F_{18}$: C, 32.68; H, 1.20; N, 3.02%. Found: C, 32.31; H, 1.31; N, 2.93%. IR (KBr) ν/cm^{-1}: 3138(vw), 2962(vw), 1665(m), 1648(s), 1605(m), 1598(mw, sh), 1578(mw), 1561(m), 1533(m), 1497(ms), 1478(m), 1465(mw, sh), 1442(mw), 1349(w), 1321(mw), 1256(s), 1207(s), 1144(s), 1100(ms), 1065(w), 1045(w), 1015(mw), 1007(w), 974(vw), 950(vw), 802(ms), 763(ms), 739(m), 660(s), 647(mw), 628(w), 585(ms), 528(mw), 465(mw), 411(w).

Sm(hfac)$_3$(bpy): mechanochemical synthesis. Sm(hfac)$_3$(H$_2$O)$_2$ (0.2002 g, 0.2479 mmol) was ground together with 2,2′-bipyridine (0.0384 g, 0.245 mmol) for approximately 20 minutes. DSC melting point 139-141 °C. IR (KBr) ν/cm^{-1}: 3136(vw), 1666(m), 1653(m, sh), 1648(s, br), 1605(mw), 1598(mw), 1579(mw), 1560(m), 1532(mw), 1496(ms), 1478(m), 1464(m, sh), 1443(mw), 1377(mw), 1366(w), 1350(w), 1321(w), 1313(vw), 1256(s), 1217(s, sh), 1207(s,br), 1146(s), 1119(vw), 1101(m), 1065(w), 1045(w), 1016(mw), 1008(w), 974(vw), 951(vw), 803(m), 799(m), 763(ms), 740(mw), 738(mw), 721(w), 660(s), 647(w), 628(w),

La(hfac)$_3$(bpy)$_2$: solution synthesis. Excess 2,2′-bipyridine (0.3010 g, 1.928 mmol) was added to a solution of La(hfac)$_3$(DME) (0.7121 g, 0.8376 mmol) in hexanes (150 mL) at room temperature with vigorous stirring. After 4 h of stirring, the colorless solution was concentrated to a white solid product, using a rotary evaporator and minimal heating. This product was recrystallized from a solution of hexanes and methylene chloride at -4 °C, generating large, colorless blocks; yield 0.4572 g (51%). M.p. (in air 760 mmHg) 198 - 200 °C. Anal. Calcd. for $LaC_{35}H_{19}N_4O_6F_{18}$: C, 39.20; H, 1.79; N, 5.22%. Found: C, 39.36; H, 1.96; N, 5.33%. IR (KBr) ν/cm^{-1}: 3138(vw), 1675(m, sh), 1656(s), 1600(mw), 1580(mw), 1551(m), 1525(ms), 1512(ms, br), 1479(m), 1437(mw), 1343(w), 1321(mw), 1259(s), 1202(s), 1143(s), 1096(m), 1063(w), 1045(w), 1008(mw), 968(vw), 949(vw), 804(w), **793**(m), 754(ms), 739(m), 660(m), 640(mw), 621(w), 582(m), 527(w), 454(vw), 447(vw), 417(w). ^{1}H NMR (400 MHz, CDCl$_3$): δ(^{1}H) = 9.17 (d, 4H, J = 4.97 Hz), 7.93 (m, 4H), 7.85 (ddd, 4H), 7.38 (ddd, 4H), 5.62 (s, 3H, hfac). ^{13}C NMR (100MHz, CDCl$_3$): δ(^{13}C) = 174.79 (q, $^2J_{C\text{-}F}$ = 33.55), 153.98, 151.06, 138.13, 123.98, 120.73, 117.59 (q, $^1J_{C\text{-}F}$ = 287.54), 88.71.

La(hfac)$_3$(bpy)$_2$: mechanochemical synthesis. La(hfac)$_3$(H$_2$O)$_3$ was ground into a fine powder (0.2051 g, 0.252 mmol) and to it was added 2,2,'-bipyridine (0.0803 g, 0.514 mmol). The mixture was ground together in an agate mortar with an agate pestle for about 30 minutes. The crude material was collected and analyzed by IR and melting point. M.p. (in air 760 mmHg) 181 – 184 °C. DSC indicated melting at 181-183 °C. IR (KBr, Nujol) ν/cm^{-1}: 3315(vw), 1656(s), 1653 (s, sh), 1648 (s, sh), 1608(vw), 1600(mw), 1579(mw, sh), 1568 (w), 1559(mw), 1550 (mw). 1533 (mw), 1525(m), 1511(ms, br), 1479(mw), 1476(mw), 1462(m, br), 1443(mw), 1437(mw), 1320(w), 1263(s), 1252(s), 1216(s), 1205(s, sh), 1194(s), 1153(s, sh), 1140(s, br), 1099(m), 1063(vw), 1045(vw), 1043(vw), 1025(w), 1008(mw), 976(vw, br), 968(vw), 953(vw), 949(vw), 805(mw), **796**(m, sh), **793**(m), 766(mw), 754(ms), 740(m), 721(vw), 664(mw), 660(m), 653(w), 640(w), 622(vw). ^{1}H NMR (500 MHz, CDCl$_3$): δ(^{1}H) = 9.11 (s, 4H), 7.98 (m, 4H), 7.86 (m, 4H), 7.38 (m, 4H), 5.67 (s, 3H, hfac). ^{13}C NMR (125 MHz, CDCl$_3$): δ(^{13}C) = 174.79 (q, $^2J_{C\text{-}F}$ = 33.55), 153.98, 151.06, 138.13, 123.98, 120.73, 117.59 (q, $^1J_{C\text{-}F}$ = 287.54), 88.71.

Ce(hfac)$_3$(bpy)$_2$: solution synthesis. 2,2′-Bipyridine (0.3803 g, 2.435 mmol) was added to a solution of Ce(hfac)$_3$(DME)$_{1.5}$ (1.0836 g, 1.2088 mmol) in hexanes (75 mL) at room temperature with vigorous stirring. A precipitate formed immediately. The suspension was stirred at room temperature for 4 h. The pale yellow solution was concentrated to a pale yellow solid, using a rotary evaporator and minimal heating; yield 1.0491 g (81%). A 0.5915 g aliquot of yellow powder was recrystallized from a solution of hexanes and methylene chloride at -4 °C to form large, bright yellow blocks; yield 0.3940 g (54%). M.p. (in air 760 mm Hg) 186 - 188 °C. Anal. Calcd. for $CeC_{35}H_{19}N_4O_6F_{18}$: C, 39.16; H, 1.78; N, 5.22%. Found: C, 39.02; H, 1.89; N, 5.24%. IR (KBr) ν/cm^{-1}: 3138(vw), 2962(vw), 2917(vw), 2845(vw), 1656(s), 1599(mw), 1580(mw), 1551(m), 1525(ms), 1511(ms), 1479(m), 1458(w), 1437(mw), 1344(w), 1320(mw), 1255(s), 1201(s), 1142(s), 1096(m), 1064(w), 1045(w), 1008(mw), 967(vw), 949(vw), 805(w), **792**(m), 754(ms), 739(m), 660(m), 640(mw), 621(w), 582(m), 527(w), 455(vw), 417(w).

Ce(hfac)$_3$(bpy)$_2$: mechanochemical synthesis. Ce(hfac)$_3$(H$_2$O)$_3$ was ground into a fine powder (0.2035 g, 0.2495 mmol) and to it was added 2,2,'-bipyridine (0.0776 g, 0.497 mmol). The mixture was ground together in an agate mortar with an agate pestle for about 15 minutes. The crude material was collected and analyzed by IR and melting point. M.p. (in air 760 mmHg) 170 - 178 °C. DSC melting point 170-174 °C. IR (KBr, Nujol) ν/cm^{-1}: 3313(vw), 1657(s), 1654(s, sh), 1648(s, sh), 1609(vw), 1600(mw), 1580(mw, sh), 1568(w), 1559(mw), 1551(mw). 1533 (mw), 1525(m), 1511(ms, br), 1479(mw), 1476(mw), 1462(m, br), 1443(mw), 1437(mw), 1365(w, sh), 1320(w), 1262(s), 1252(s), 1216(s), 1205(s, sh), 1194(s), 1153(s, sh), 1140(s, br), 1099(m), 1064(vw), 1060(vw), 1046(vw), 1043(vw), 1025(w), 1008(mw), 977(vw, br), 968(vw), 952(vw), 949(vw), 805(mw), **796**(m, sh), **793**(m), 766(mw), 754(ms), 740(m), 721(vw, br), 664(mw), 660(m), 653(w), 640(w), 622(vw).

Pr(hfac)$_3$(bpy)$_2$: solution synthesis. 2,2′-Bipyridine (1.22 g, 7.81 mmol) was added to a solution of Pr(hfac)$_3$(DME) (3.25 g, 3.81 mmol) in hexanes (150 mL) at room temperature with vigorous stirring. A pale green precipitate formed immediately. The suspension was stirred at room temperature for 2 h. The pale green solution was concentrated to a pale green solid, using a rotary evaporator and minimal heating. The crude yield was quantitative. A 0.7584 g aliquot of green powder was recrystallized from a solution of hexanes and methylene chloride at -4 °C to form large, bright green blocks; yield 0.4540 g (60%). M.p. (in air 760 mmHg) 174 - 176 °C. Anal. Calcd. for PrC$_{35}$H$_{19}$N$_4$O$_6$F$_{18}$: C, 39.13; H, 1.78; N, 5.21%. Found: C, 39.13; H, 1.90; N, 5.33%. IR (KBr) ν/cm^{-1}: 3314(vw), 3138(vw), 3077(vw), 3045(vw), 1656(s), 1600(mw), 1580(mw), 1568(w), 1551(m), 1525(ms), 1512(ms), 1479(m), 1437(m), 1343(w), 1320(mw), 1255(s), 1201(s), 1140(s), 1098(m), 1064(w), 1045(w), 1008(mw), 969(w), 949(w), 805(mw), **792**(m), 754(ms), 739(m), 660(m), 640(mw), 621(w), 582(m), 527(mw), 455(vw), 419(w).

Pr(hfac)$_3$(bpy)$_2$: mechanochemical synthesis. Pr(hfac)$_3$(H$_2$O)$_3$ was ground into a fine powder (0.2510 g, 0.3080 mmol) and to it was added 2,2,’-bipyridine (0.0968 g, 0.620 mmol). The mixture was ground together in an agate mortar with an agate pestle for about 30 minutes. The crude material was collected and analyzed by IR and melting point. M.p. (in air 760 mmHg) 160 - 168 °C. DSC melting point 164-166 °C. IR (KBr, Nujol) ν/cm^{-1}: 3317(vw), 3140(vw), 1657(s), 1609(w), 1599(mw), 1579(mw), 1569(w), 1559(w), 1551(mw), 1533(mw), 1525(m), 1511(ms,br), 1480(m), 1476(mw), 1463(mw,br), 1443(mw), 1437(mw), 1377(w), 1349(vw), 1320(w), 1261(s), 1253(s), 1206(ms,sh), 1194(s), 1174(mw), 1151(s), 1141(s,br), 1100(m), 1072(w), 1065(w), 1046(vw), 1043(vw), 1024(w), 1008(mw), 970(vw), 969(vw), 949(vw), 805(w), **796**(m), **792**(ms), 766(mw), 754(ms), 739(mw), 722(vw), 664(mw,sh), 661(m), 653(w), 640(mw), 633(vw), 622(vw).

Nd(hfac)$_3$(bpy)$_2$: solution synthesis. 2,2′-Bipyridine (0.0826 g, 0.529 mmol) was added to a solution of Nd(hfac)$_3$(DME) (0.2126 g, 0.2485 mmol) in hexanes (15 mL) at room temperature with vigorous stirring. The pale blue suspension was stirred at room temperature for 4 h, concentrated to a blue-purple solid using a rotary evaporator and minimal heating and immediately introduced into a glovebox under dry argon atmosphere; yield 0.2225 g (83%). Analytically pure material was prepared by recrystallization from a 4:1 mixture of hexanes and toluene; yield 0.1725 g (64%). M.p. (inert atmosphere) 168 - 169 °C. IR (Nujol, NaCl) ν/cm^{-1}: 3139 (vw), 1656 (s), 1599 (w), 1580 (w), 1551 (w), 1525 (m), 1521 (m), 1492 (vw), 1464 (s), 1377 (s), 1344 (vw), 1320 (w), 1254 (s), 1191 (s), 1141 (s), 1098 (w), 1065 (vw), 1046 (vw), 1008 (w), 970 (vw), 949 (vw), 888 (vw), 805 (vw), **792** (m), 754 (s), 739 (m), 720 (vw), 660 (m), 639 (w), 581 (vw). Anal. Calcd for NdC$_{35}$H$_{19}$N$_4$O$_6$F$_{18}$: C, 39.01; H, 1.78; N, 5.20%; Found: C, 39.01; H, 1.86; N, 5.14%.

Nd(hfac)$_3$(bpy)$_2$: mechanochemical synthesis. Nd(hfac)$_3$(H$_2$O)$_3$ was ground into a fine powder (0.2504 g, 0.3060 mmol) and to it was added 2,2′-bipyridine (0.0956 g, 0.612 mmol). The mixture was ground together in an agate mortar with an agate pestle for about 30 minutes. The crude material was collected and analyzed by IR and melting point. M.p. (in air 760 mm Hg) 151 - 153 °C. DSC melting point 154-156 °C. IR (KBr, Nujol) ν/cm^{-1}: 3309(vw), 3297(vw) 3136(vw), 1658(m), 1651(m,sh), 1609(vw), 1600(w), 1580(vw), 1567(vw), 1559(vw), 1552(vw), 1533(w,sh), 1526(mw), 1511(mw, br), 1480(w), 1466(m, br), 1457(mw), 1443(w), 1438(w), 1377(w), 1366(vw), 1319(vw), 1259(ms), 1254(ms), 1207(m,sh), 1194(ms), 1151(s), 1139(sh,s), 1101(m), 1065(vw), 1043(vw), 1024(vw), 1013(vw), 1009(vw), 976(vw), 950(vw), 805(w), **797**(m), **793**(mw, sh), 766(mw), 754(m), 739(mw), 721(vw), 665(mw,sh), 661(m), 653(vw), 640(vw), 621(vw).

Sm(hfac)$_3$(bpy)$_2$: solution synthesis. Under argon atmosphere, 2,2′-bipyridine (0.1165 g, 0.7459 mmol) was added to a solution of Sm(hfac)$_3$(DME) (0.3211 g, 0.3727 mmol) in dry hexane (100 mL) at room temperature with vigorous stirring. A pale beige-yellow precipitate formed immediately. The suspension was stirred at room temperature under Ar for 2 h, then the solvent was removed under reduced pressure. The resulting pale beige-yellow powder was recrystallized under Ar atmosphere from a solution of dry hexane and dry toluene to form large pale beige blocks; yield 0.1002 g (25%). M.p. (inert atmosphere 760 mmHg) 119 - 122 °C. Anal. Calcd. for SmC$_{35}$H$_{19}$N$_4$O$_6$F$_{18}$: C, 39.13; H, 1.78; N, 5.21%. Found: C, 39.13; H, 1.90; N, 5.33%. IR (Nujol, NaCl) ν/cm^{-1}: 3309(vw), 3134(vw), 1658(s), 1599(mw), 1580(mw), 1552(m), 1525(m), 1514(m), 1492(mw), 1479(m), 1464(ms), 1438(m), 1377(m), 1345(w), 1319(mw), 1254(s), 1201(s), 1143(s), 1100(m), 1065(w), 1046(w), 1008(mw), 970(vw), 950(w), 804(mw), **792**(m), 754(ms), 740(m), 660(ms), 639(mw), 619(w), 583(ms).

[Sm(hfac)$_3$(bpy)(H$_2$O)]·bpy: mechanochemical synthesis. Sm(hfac)$_3$(H$_2$O)$_2$ was ground into a fine powder (0.2026 g, 0.2509 mmol) and to it was added 2,2,’-bipyridine (0.0838 g, 0.536 mmol). The mixture was ground together in an agate mortar with an agate pestle for about 30 minutes in air. The crude material was collected and analyzed by IR and melting point. Crude material m.p. (in air 760 mmHg) 108 - 111 °C. DSC melting point 113 - 116 °C. IR (KBr, Nujol) ν/cm^{-1}: 3301(vw), 3137(w), 1663(m,sh), 1653(ms), 1608(vw), 1599(w), 1596(w), 1589(vw), 1577(w), 1560(mw), 1554(mw) 1534(m), 1528(m,br), 1507(ms), 1465(s,br), 1457(s), 1443(m), 1421(w), 1378(w), 1349(vw,br), 1319(vw), 1255(s), 1212(s), 1195(s), 1150(s, sh), 1139(s), 1100(mw), 1067(vw), 1043(vw), 1024(w), 1012(w), 1000(vw), 977(vw), 951(vw), 946(vw), 892(vw), 805(mw), **797**(m), 766(m), 756(mw), 739(mw), 721(w), 661(m), 653(w), 643(vw), 632(vw), 624(vw), 621(vw).

Conclusions

We have demonstrated stoichiometric control of the coordination number for lanthanide trications La, Ce, Pr, Nd, and Sm with common bidentate ligands. The complete 8-coordinate Ln(hfac)$_3$(bpy) and 10-coordinate Ln(hfac)$_3$(bpy)$_2$ series are reported. Careful handling and the use of anhydrous precursors are required to obtain 10-coordinate complexes of the later lanthanides and 8-coordinate complexes of the earlier lanthanides, both of which are subject to decomposition upon exposure to atmospheric moisture. Our observations regarding moisture-sensitivity are in keeping with the preference for decreasing coordination numbers with decreasing lanthanide ion size.

Mechanochemical synthesis from hydrate precursors is shown to be a quicker and greener route to those complexes that are air-stable. Complete displacement of water to generate a single-component product in air was only observed for the 8-coordinate Sm(hfac)$_3$(bpy) complex. Surprisingly, under dry atmosphere, the 10-coordinate Sm(hfac)$_3$(bpy)$_2$ is clearly observed in the product mixture, indicating that a mechanochemical approach is viable for displacement of water, even for moisture sensitive products, under the right conditions. Furthermore, grinding in the presence of KBr appears to favor the anhydrous product. Future access to air-tight ball-milling vials is anticipated to provide an improved approach to the mechanochemical synthesis of moisture-sensitive species.

Conflict of Interest

The authors declare no conflict of interest.

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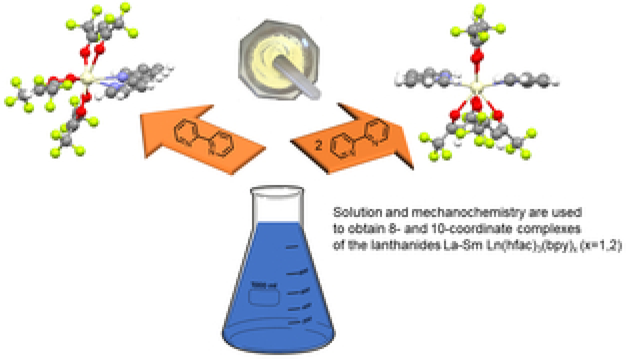

Solution and mechanochemistry are used to obtain 8- and 10-coordinate complexes of the lanthanides La-Sm Ln(hfac)$_3$(bpy)$_x$ (x=1,2)

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