Supplementary Data

			ν_{OH}	V _{NO}			V _{PO}
	x	У		ν ₅	ν_1	v ₂	
L							1107
La	1	2	3481 3282	1459 1444	1298 1280	1028	1065
Nd	1	2	3502 3278	1460 1447	1303 1281	1030	1067
Sm	0	0.5	3392	1511 1458	1305 1278	1031	1063
Eu	0	1	3407	1508 1456	1305 1277	1021	1066
Dy	0	0		1507 1470	1274	1021	1073
Er	0	0		1512 1472	1283	1024	1070
Lu	0	0		1512 1471	1280	1022	1085

Table S1 Principle infrared bands (cm⁻¹) for Ln(NO₃)₃(^tBu₃PO)₂(H₂O)_x(EtOH)_y

Table S2 ESMS data for the principle metal containing ions from $Ln(NO_3)_3L_2$ in CH_2Cl_2 /MeCN Observed (calculated)

La	Nd	Sm	Eu	Dy	Er	Lu
917.4209	922.4265	930.4348	931.4364	942.4451	944.4475	953.4552
(917.4213)	(922.4227)	(930.4347)	(931.4362)	(942.4694)	(944.4452)	(953.4557)
872.4368	877.4422	885.4503	886.4521	897.4605	901.4627	908.4701
(872.4362)	(877.4376)	(885.4496)	(886.4511)	(897.4590)	(901.4602)	(908.4706)
699.2403	704.2459	712.2545	713.2560	724.2644	726.2643	735.2747
(699.2414)	(704.2456)	(712.2547)	(713.2562)	(724.2642)	(726.2653)	(735.2758)
Not obs		552.3183	552.8192	558.3234	560.3244	563.8282
	(547.3127)	(522.3187)	(552.8195)	(558.3234)	(560.3240)	(563.8292)
426.2291	428.7319		433.2367	437.3673		444.7472
405.2241	407.7219	411.7308	412.2315	417.7358	419.7370	423.2411
(405.2242)	(407.7249)	(411.7309)	(412.2317)	(417.7356)	(419.7362)	(423.2414)
	La 917.4209 (917.4213) 872.4368 (872.4362) 699.2403 (699.2414) Not obs 426.2291 405.2241 (405.2242)	LaNd917.4209 (917.4213)922.4265 (922.4227)872.4368 (872.4362)877.4422 (877.4376)699.2403 (699.2414)704.2459 (704.2456)Not obs(547.3127)426.2291428.7319405.2241 (405.2242)407.7219 (407.7249)	LaNdSm917.4209 (917.4213)922.4265 (922.4227)930.4348 (930.4347)872.4368 (872.4362)877.4422 (877.4376)885.4503 (885.4496)699.2403 	LaNdSmEu917.4209 (917.4213)922.4265 (922.4227)930.4348 (930.4347)931.4364 (931.4362)872.4368 (872.4362)877.4422 (877.4376)885.4503 (885.4496)886.4521 (886.4511)699.2403 (699.2414)704.2459 (704.2456)712.2545 (712.2547)713.2560 (713.2562)Not obs(547.3127)552.3183 (522.3187)552.8192 (552.8195)426.2291428.7319433.2367405.2241 (405.2242)407.7219 (407.7249)411.7308 (411.7309)412.2315 (412.2317)	LaNdSmEuDy917.4209 (917.4213)922.4265 (922.4227)930.4348 (930.4347)931.4364 (931.4362)942.4451 (942.4694)872.4368 (872.4362)877.4422 (877.4376)885.4503 (885.4496)886.4521 (886.4511)897.4605 (897.4590)699.2403 (699.2414)704.2459 (704.2456)712.2545 (712.2547)713.2560 (713.2562)724.2644 (724.2642)Not obs(547.3127)552.3183 (522.3187)552.8192 (552.8195)558.3234 (558.3234)426.2291428.7319433.2367 (407.7249)411.7308 (411.7309)412.2315 (412.2317)417.7358 (417.7356)405.2241 (407.7249)407.7249 (407.7249)411.7308 (411.7309)412.2315 (412.2317)417.7358 (417.7356)	LaNdSmEuDyEr917.4209 (917.4213)922.4265 (922.4227)930.4348 (930.4347)931.4364 (931.4362)942.4451 (942.4694)944.4475 (942.4694)872.4368 (872.4362)877.4422 (877.4376)885.4503 (885.4496)886.4521 (886.4511)897.4605 (897.4590)901.4627 (901.4602)699.2403 (699.2414)704.2459 (704.2456)712.2545 (712.2547)713.2560 (713.2562)724.2644 (724.2642)726.2643 (726.2653)Not obs (547.3127)552.3183 (522.3187)552.8192 (552.8195)558.3234 (558.3234)560.3244 (560.3240)405.2241 (405.2242)407.7219 (407.7249)411.7308 (411.7309)412.2315 (412.2317)417.7358 (417.7356)419.7370 (419.7362)

			Temperature /°C				
-	nucleus		20	-30	-60	-90	
	³¹ P		78.69	77.34	76.97	$76.93(4)^{c}$	
						76.29(1)	
						73.56(1)	
	$^{13}C^{a}$	С	39.58(d)	39.19(d)	38.84(d)	38.50(d)	
La		CH ₃	28.80	28.45	28.06	$28.84(2)^{c}$	
						25.33(1)	
	$^{1}\mathrm{H}^{\mathrm{b}}$		1.389(d)	1.341(d)	1.309(d)	1.282(s)	
		•					
	³¹ P		194.50	229.50	251.85	$277.64(8)^{c}$	
						287.99(1)	
	^{13}C	С	42.45(d)	44.17(br,s)	45.10(br,s)	44.78(br,s)	
		CH ₃	31.47	32.93	33.75	34.97	
	1 H		3.742	4.7463	5.211	6.606	
Nd						5.864	
						4.908	
	1.21	1	T	1	1	1	
	⁵¹ P		72.26	73.54	75.66	$78.56(10)^{\circ}$	
						81.77(1)	
						79.61(1)	
	12 0					72.60(1)	
~	$^{15}C^{a}$	C	39.84(d)	39.90(d)	39.72 (d)	39.48(d)	
Sm		CH ₃	28.37	28.59	28.53	29.75	
	1b					25.72	
	¹ H ⁰		1.570(d)	1.486(d)	1.438(d)	1.329(s)	
	31-	1		07.74	10-11	100.77	1
	Ч		-57.66	-85.54	-107.46	-133.57	
En							
Eu	13 C^a	C	27.77(d)	34.0	30.0	26.5	
		CH.	25.52	22.03	20.70	10.50	
	1 H p		1 338(d)	$\frac{22.75}{3.17(s)}$	$\frac{20.77}{4.74(s)}$	6 67(s)	
	11		[1.550(u)	-3.17(8)	-4.74(3)	-0.07(3)	
	³¹ P		620.2	1033 5	1429.0	2052 1	
Dv	^{13}C	С	388.8	605.4	Not obs	Not obs	
2,		CH ₂	207.2	324.5	Not obs	Not obs	
	1 H		207.2	-0.55	-1 1	-1 2	
	11			0.55	1.1	1.2	
<u> </u>	³¹ P		-267.4	-391.8	-498.4	-657.1	
Er	¹³ C	С	-32.5	-65.9	-97.2	Not obs	
	-	CH ₃	-14.9	-35.0	-53.4	-68.6	
	$^{1}\mathrm{H}$,	19.98	6.04	-6.78	-23.11	
		1					1
<u> </u>	³¹ P		80.21	79.50	79.07	78.66	
Lu	$^{13}C^{a}$	С	39.82(d)	39.47(d)	39.46(d)	39.45(d)	1
	-	CH ₃	28.65	28.26	28.29	29.47.	
L	1					7	1

Table S3 NMR data for Ln(NO₃)₃^{(t}Bu₃PO)₂ in CD₂Cl₂

				25.58	
${}^{1}\mathrm{H}^{\mathrm{b}}$	1.393(d)	1.334(d)	1.307(d)	1.271(s)	

a. ${}^{1}J_{PC} \sim 49$ Hz b. ${}^{3}J_{PH} \sim 13.5$ Hz c. Relative intensities

Table of Contents entry

Lanthanide nitrate complexes with ${}^{t}Bu_{3}PO$ (=L) form 1:2 complexes $Ln(NO_{3})_{3}L_{2}$ rather than the more common $Ln(NO_{3})_{3}L_{3}$ found with other trialkylphosphine oxides. The complexes of the heavier lanthanides (Ln = Dy, Er and Lu) crystallise with two isomers in the solid state. These are not observable as separate species in solution and show no evidence of interconversion in the solid state. Attempts to prepare pure 1:3 complexes [Ln(NO_{3})_{2}L_{3}]^{+} were not successful.

