ESI

Trivalent Scandium, Yttrium and Lanthanide Complexes with Thia-oxa and Selena-oxa Macrocycles and Crown Ether Coordination

Martin J. D. Champion, Paolo Farina, William Levason* and Gillian Reid

Preparations:

[LaI_3(15-crown-5)]: To a Schlenk flask containing a suspension of LaI_3 (0.150 g, 0.29 mmol) in MeCN (10 mL) was added a solution of 15-crown-5 (0.070 g, 0.32 mmol) in MeCN (10 mL). A white precipitate began forming immediately and the suspension was stirred for a further 30 mins. The precipitate was filtered off and dried under vacuum. Yield: 0.110 g, 52%. Required for $C_{10}H_{20}I_3LaO_5 \cdot 0.5MeCN$ (760.4): C, 17.4; H, 2.9; N, 0.9. Found: C, 17.7; H, 3.6; N, 0.7%. ^{1}H NMR (CD_3CN, 295 K): δ = 4.29 (m, [10H]) 4.10 (m, [10H]).

[LaI_3(18-crown-6)]: To a Schlenk flask containing a suspension of LaI_3 (0.10 g, 0.19 mmol) in dichloromethane (30 mL) was added a solution of 18-crown-6 (0.051 g, 0.19 mmol) in dichloromethane (30 mL). The solution was stirred for 72 h and the residual solid filtered off. The filtrate was taken to dryness under vacuum. The residue was washed with diethyl ether (10mL) leaving a yellow powder. Yield 0.06 g, 40%. Required for $C_{12}H_{24}I_3LaO_6$ (783.9): C, 18.4; H, 3.1. Found: C, 18.5; H, 3.2%. ^{1}H NMR (CD_2Cl_2, 295 K): δ = 4.26 (s).

[LaI_2(18-crown-6)]PF_6 : To a Schlenk flask containing a suspension of LaI_3 (0.150 g, 0.29 mmol) in MeCN (10 mL) was added a solution of 18-crown-6 (0.076 g, 0.29mmol) in MeCN (10 mL). The solution was stirred for 1 h after which a small amount of extremely fine solid was filtered off. $[NH_4]PF_6$ (0.047 g, 0.29 mmol) in methanol (3 mL) was added and stirred for a further 1 h. The solvent volume was reduced by half, diethyl ether (20 mL) was added and the solution placed in the freezer overnight. This produced a white powder which was collected by filtration and dried under vacuum. Yield: 0.165 g, 71%. Required for $C_{12}H_{24}F_6I_2LaO_6P$ (802.0): C, 18.0; H, 3.0. Found: C, 17.7; H, 3.6%. ^{1}H NMR (CD_3CN, 295 K): δ = 4.17 (s). $^{19}F\{^1H\}$ NMR (CD_3CN, 295 K): δ = −72.3 (d, $^1J_{FP}$ = 702 Hz). Λ_M MeCN 10^{-3} mol dm^{-3} = 272 Ω^{-1} cm^2 mol^{-1}. IR (Nujol/ cm^{-1}): 845 (vs), 558(m) (PF_6).

[LuI_2(15-crown-5)]I: To a Schlenk flask containing a suspension of LuI_3 (0.075 g, 0.135 mmol) in MeCN (5 mL) was added a solution of 15-crown-5 (0.036 g, 0.135 mmol) in MeCN (5 mL). The solution was stirred for 1 h after which a small amount of extremely fine precipitate was filtered off. Diethyl ether (10 mL) was layered onto the solution. Colourless crystals were deposited overnight, along with some powdered material. The solid was collected by filtration and dried under vacuum. Yield: 0.122 g, 58%. Required for $C_{10}H_{20}I_3LuO_5$ (776.0): C, 15.5; H, 2.6. Found: C, 15.5; H, 2.5%. ^{1}H NMR (CD_3CN, 295 K): δ = 4.39 (s).

[LuI (18-crown-6)(MeCN)$_2$]I$_2$: was made similarly from LuI_3 (0.075 g, 0.135 mmol) and 18-crown-6 (0.036 g, 0.135mmol). Yield: 0.055 g, 45%. Required for $C_{16}H_{30}N_2I_3LuO_6$ (861.1): C, 21.3; H, 3.4; N, 3.1. Found: C, 21.5; H, 3.5; N, 3.2%. ^{1}H NMR (CD_3CN, 295 K): δ = 4.22 (s). IR (Nujol/ cm^{-1}): 2308, 2274 (MeCN).

[NdI$_3$(18-crown-6)]: was made similarly from NdI_3 (0.152 g, 0.29 mmol) and 18-crown-6 (0.076 g, 0.29 mmol). Yield 0.10 g, 44%. Required for $C_{12}H_{24}I_3NdO_6$ (789.3): C, 18.3; H, 3.1. Found: C, 17.9; H, 3.0%. ^{1}H NMR (CD_3CN, 295 K): δ = 8.53 (s). Λ_M MeCN, 10^{-3} mol dm^{-3}: 288 Ω^{-1} cm^2 mol^{-1}.

[CeI$_3$(18-crown-6)]: was made similarly. Small colourless crystals grew overnight from the filtrate. The crystals were collected by filtration and dried under vacuum. Yield 0.086 g, 38%. Required for $C_{12}H_{24}CeI_3O_6$ (785.2): C, 18.4; H, 3.1. Found: C, 18.6; H, 3.7%. ^{1}H NMR (CD_3CN, 295 K): δ = 6.92 (s). Λ_M MeCN, 10^{-3} mol dm^{-3} : 240 Ω^{-1} cm^2 mol^{-1}.

[La(O$_3$SCF$_3$)$_2$(18-crown-6)][O$_3$SCF$_3$]: In a Schlenk flask containing $La(O_3SCF_3)_3$ (0.100 g, 0.17 mmol) was added a solution of 18-crown-6 (0.161 g, 0.61 mmol) in MeCN (20 mL). The resulting white suspension was stirred overnight at which point a clear solution had been obtained. The solvent was removed under vacuum and then residue was triturated with dichloromethane (10 mL) and hexane (5 mL). The white microcrystalline product was collected by filtration and dried under vacuum. Yield: 0.060 g, 44%. Required for $C_{15}H_{24}F_9LaO_{15}S_3$ (850.4): C, 21.2; H, 2.8. Found: C, 21.3; H, 3.1%. ^{1}H NMR (CD_3CN, 295 K) δ = 4.05 (s). ^{19}F{^{1}H} NMR (CD_3CN, 295 K) δ = −78.4 (s). ^{139}La NMR (CH_3CN/CD_3CN, 295 K): δ = −112.4 ($W_{1/2}$ = 3000 Hz). Λ_M MeCN, 10^{-3} mol dm^{-3} : 163 Ω^{-1} cm^2 mol^{-1}.

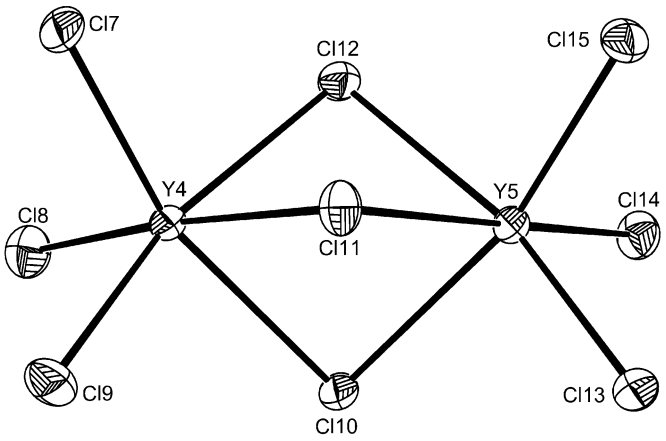

Figure S1. The anion in $[YCl_2(18\text{-crown-6})]_3[Y_2Cl_9]$. Y−Cl (terminal) = 2.5317(15) – 2.5709(14), Y–Cl (bridge) = 2.7091(14) – 2.7468(15) Å.

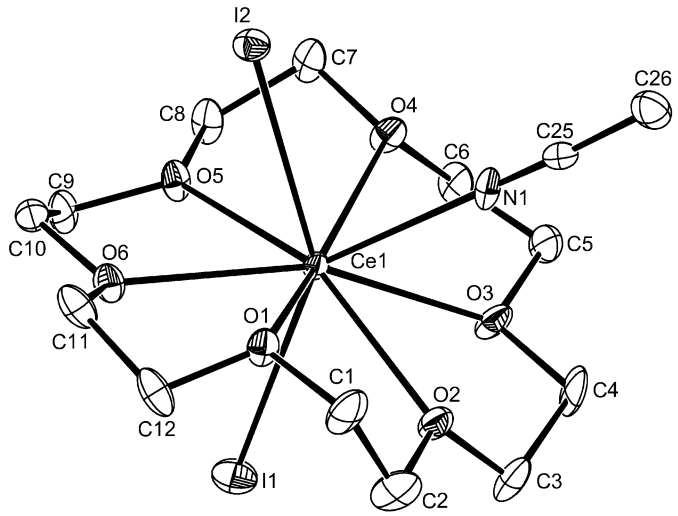

Figure S2. The cation in $[CeI_2(18\text{-crown-6})(MeCN)]I\cdot n MeCN$ (n = 1/2). The displacement ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ce1−O5 = 2.550(5), Ce1−1 = 2.576(5), Ce1−O2 = 2.582(5), Ce1−O4 = 2.589(5), Ce1−O6 = 2.597(5), Ce1−N1 = 2.608(7), Ce1−O3 = 2.622(5), Ce1−I1 = 3.1886(9), Ce1−I2 = 3.2103(8), O1−Ce1−O2 = 62.82(17), O5−Ce1−O4 = 62.55(17), O1−Ce1−O6 = 2.35(17), O2−Ce1−O3 = 60.55(17), O4−Ce1−O3 = 61.79(17), N1−Ce1−I1 = 141.14(16), N1−Ce1−I2 = 70.46(16), I1−Ce1−I2 = 147.62(2). Ce(2) is very similar.

Table S1: Crystallographic parameters

Compound	$[LaI_3([18]aneO_4S_2)]$	$[LaI(OH_2)_2([18]aneO_4S_2)]I_2 \cdot H_2O$	$[LaI_3([18]aneO_4Se_2)]$	$[LaI_3(15\text{-crown-}5)] \cdot MeCN$	$[LaI_2(18\text{-crown-}6)(MeCN)]I \cdot n MeCN$ (n = 0.5)	$[CeI_2(18\text{-crown-}6)(MeCN)]I \cdot n MeCN$ (n = 0.5)
Formula	$C_{12}H_{24}I_3LaO_4S_2$	$C_{12}H_{30}I_3LaO_7S_2$	$C_{12}H_{24}I_3LaO_4Se_2$	$C_{12}H_{23}I_3LaNO_5$	$C_{15}H_{28.5}I_3LaN_{1.5}O_6$	$C_{15}H_{28.5}CeI_3N_{1.5}O_6$
M	816.04	870.09	909.84	780.92	845.50	846.71
crystal syst	Orthorhombic	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic
Space group	Pbca (no. 61)	$P2_1/c$ (no. 14)	Pbca (no. 61)	Pnma (no. 62)	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)
a [Å]	15.276(3)	8.5208(16)	15.375(3)	21.695(7)	8.1091(11)	8.0939(18)
b [Å]	13.763(2)	20.401(4)	13.506(3)	12.454(4)	21.599(3)	21.505(5)
c [Å]	20.617(4)	14.616(3)	21.053(4)	7.900(3)	29.150(4)	29.104(7)
α [deg]	90	90	90	90	90	90
β [deg]	90	106.278(3)	90	90	91.469(3)	91.479(3)
γ [deg]	90	90	90	90	90	90
U [Å^3]	4334.3(13)	2438.9(8)	4371.8(14)	2134.6(12)	5103.9(12)	5064.3(19)
Z	8	4	8	4	8	8
μ(Mo Kα) [mm^{-1}]	6.448	5.746	9.533	6.357	5.330	5.482
total no. reflns	20061	11038	23251	10231	23074	22455
unique reflns	4952	5520	5010	2541	11528	11504
R_{int}	0.149	0.174	0.073	0.136	0.032	0.073

no. of params, restraints	194, 6	226, 0	199, 0	127, 11	481, 0	481, 0
R_1[b] [$I_o > 2\sigma(I_o)$]	0.043	0.067	0.033	0.054	0.028	0.059
R_1 [all data]	0.047	0.069	0.043	0.058	0.035	0.078
wR_2[b] [$I_o > 2\sigma(I_o)$]	0.110	0.171	0.068	0.136	0.052	0.107
wR_2 [all data]	0.113	0.175	0.073	0.140	0.054	0.115

[a] Common items: temperature = 100 K check; wavelength (Mo–Kα) = 0.71073 Å; θ(max) = 27.5°; [b] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$.

Table S1 cont.

Compound	$[LuI_2([18]aneO_4Se_2)]I\cdot n$MeCN ($n$ = 2)	$[Lu(MeCN)_2(OH_2)(15\text{-crown-}5)]I_3$	$[LuI(MeCN)_2(18\text{-crown-}6)]\ I_2$	$[YCl_2([18]aneO_4S_2)][FeCl_4]$	$[YCl_2(18\text{-crown-}6)]_3\ [Y_2Cl_9].n$MeCN (n =1.65)
Formula	$C_{16}H_{30}I_3LuN_2O_4Se_2$	$C_{14}H_{28}I_3LuN_2O_6$	$C_{16}H_{30}I_3LuN_2O_6$	$C_{12}H_{24}Cl_6FeO_4S_2Y$	$C_{39.30}H_{76.95}Cl_{15}N_{1.65}O_{18}Y_5$
M	1028.01	876.05	902.09	653.89	1836.98
crystal syst	Orthorhombic	Orthorhombic	Monoclinic	Orthorhombic	Triclinic
Space group	Pnma (no. 62)	Pnma (no.62)	$P2_1/m$ (no. 11)	Pccn (no. 56)	P-1 (no. 2)
a [Å]	15.436(5)	18.946(7)	8.787(4)	23.764(5)	13.174(2)
b [Å]	11.954(4)	11.146(4)	10.151(4)	16.180(2)	17.299(3)
c [Å]	14.804(5)	11.901(5)	14.970(6)	12.5376(18)	18.224(4)
α [deg]	90	90	90	90	115.694(3)
β [deg]	90	90	100.635(5)	90	95.928(5)
Γ [deg]	90	90	90	90	91.622(1)
U [Å^3]	2731.6(15)	2513.1(16)	1312.4(9)	4820.7(14)	3710.0(12)
Z	4	4	2	8	2
μ(Mo Kα) [mm^{-1}]	9.691	7.640	7.319	3.851	4.463
total no. reflns	11879	12417	6255	41731	45947
unique reflns	3265	3019	3155	5515	17003
R_{int}	0.154	0.125	0.1977	0.0503	0.1446
no. of params,	148, 6	128, 0	137, 0	235, 0	731, 6

restraints					
R_1[b] [$I_o > 2\sigma(I_o)$]	0.0630	0.0410	0.0868	0.0301	0.0647
R_1 [all data]	0.0716	0.0440	0.0868	0.0419	0.0769
wR_2[b] [$I_o > 2\sigma(I_o)$]	0.1529	0.1038	0.2166	0.0627	0.1807
wR_2 [all data]	0.1595	0.1061	0.2166	0.0664	0.1920

Table S1 cont.

Compound	$[ScI_2([18]aneO_4S_2)]I \cdot MeCN$	$[ScCl_2([18]aneO_4S_2)][FeCl_4]$
Formula	$C_{14}H_{27}I_3NO_4S_2Sc$	$C_{12}H_{24}Cl_6FeO_4S_2Sc$
M	763.15	609.94
crystal syst	Orthorhombic	Orthorhombic
Space group	Pnma (no.62)	Abm2 (no. 69)
A [Å]	15.2900(10)	16.150(4)
B [Å]	11.9434(8)	64.370(8)
C [Å]	14.4913(8)	11.3327(12)
α [deg]	90	90
β [deg]	90	90
Γ [deg]	90	90
U [$Å^3$]	2646.3(3)	11781(4)
Z	4	20
μ(MoKα) [mm^{-1}]	3.951	1.777
total no. reflns	27355	69707
unique reflns	2710	13386
R_{int}	0.0610	0.0841
no. of params, restraints	144,8	428, 10
R_1[b] [$I_o > 2\sigma(I_o)$]	0.074	0.0963
R_1 [all data]	0.100	0.1288
wR_2[b] [$I_o > 2\sigma(I_o)$]	0.188	0.2292
wR_2 [all data]	0.206	0.2517