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Review

Anhydrous scandium, yttrium, lanthanide and actinide halide complexes with neutral oxygen and nitrogen donor ligands

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Dedicated to (the late) Prof. Liliane G. Hubert-Pfalzgraf.

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Abbreviations: bipy, 2,2′-bipyridine; bipyO$_2$, 2,2′-bipyridine *N*,*N*′ dioxide; btp, bicapped trigonal prismatic; deg, diethylene glycol; depa, *N*,*N*-diethylpropionamide; de-hipp, diethyl α-hydroxyiminopropylphosphonates; dip-hipp, diisopropyl α-hydroxyiminopropylphosphonates; dh, dodecahedral; dma, *N*,*N*-dimethylacetamide; dme, dimethoxyethane; dmf, dimethylformamide; dmi, 1,3-dimethyl-2-imidazolidinone; dmpu, dimethylpropyleneurea; dmpva, *N*,*N*-dimethylpivalamide; dmso, dimethylsulphoxide; diglyme, diethyleneglycoldimethylether; ebdpao, ethane-1,2-diyl-bis(diphenylarsine) oxide; hb, hexagonal bipyramidal; hdh, hendecahedral; hmpa, hexamethylphosphoramide; Me-btp, 2,6-*bis*-(5,6-dimethyl-1,2,4-triazin-3-yl)pyridine; mhp, monocapped hexagonal planner; moh, monocapped octahedral; msa, monocapped square antiprismatic; mtp, monocapped trigonal prismatic; ntb, *tris*-(benzimidazol-2-ylmethyl)amine; N-MeIm, *N*-methylimidazole; oh, octahedral; omppa, octamethyl pyrophosphoramide; pb, pentagonal bipyramidal; Pr^n-btp, 2,6-*bis*-(5,6-dipropyl-1,2,4-triazin-3-yl)pyridine; peg, pentaethylene glycol; ptmpa, phenyltetramethylphosphoramide; py, pyridine; pybox, pyridine-2,6-bis(oxazolines); sa, square antiprismatic; ta, trigonal antiprismatic; tb, trigonal bipyramidal; tbpa, *tris*-[(2,2′-bipyridine-6-yl)methyl]amine; teao, triethylarsenic oxide; teg, tetraethylene glycol; terpy, 2,2′:6′,2″-terpyridine; tetraglyme, tetraethyleneglycoldimethylether; tipc, tetraisopropylpyridine-2,6-dicarboxamide; tma, trimethylamine; tmeda, tetramethylethylenediamine; tmpo, trimethylphosphine oxide; tmu, tetramethylurea; triglyme, triethyleneglycoldimethylether; treg, triethylene glycol; tpa, *tris*-[(2-pyridyl)methyl]amine; tpaam, *tris*-[6-{(2-*N*,*N*-diethylcarbamoyal)pyridyl}methyl]amine; tpao, triphenylarsenic oxide; tpyta, 2,4,6-*tris*(2-pyridyl)-1,3,5-triazine; tpza, *tris*-[(2-pyrazinyl)methyl]amine; tpzcn, *N*,*N*,*N*,*N*-*tetrakis*-[(2-pyrazinylmethyl]-*trans*-1,2-cyclohexanediamine; tpzen, *N*,*N*,*N*,*N*-*tetrakis*-[(2-pyrazinyl)methyl]ethylene-diamine; tpztn, *N*,*N*,*N*,*N*-*tetrakis*-[(2-pyrazinyl)methyl] trimethylenediamine; thf, tetrahydrofuran; Me$_3$[6]aneN$_3$, 1,3,5-trimethyl-1,3,5-triazacyclohexane; Me$_3$[9]aneN$_3$, 1,4,7-trimethyl-1,4,7-triazacyclononaane; HC(Me$_2$pz)$_3$, *tris*-(3,5-dimethylpyrazolyl)methane; MeSi(Me$_2$pz)$_3$, *tris*-(3,5-dimethylpyrazolyl)methylsilane; (Me$_2$pz)$_6$Cytp, *hexakis*-(3,5-dimethylpyrazolyl)cyclotriphosphazene; ttp, tricapped trigonal prismatic; tppo, triphenyl phosphine oxide; typrpo, *tris*-(pyrrolidinyl)phosphine oxide.

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Abstract

Studies on lanthanide and actinide halide complexes with neutral O- and/or N-donor ligands have intensified in recent years due to their implications in homogeneous catalysis, magnetic and optical materials, as synthons for the synthesis of novel coordination and organometallic compounds and, for Ln(II) halide complexes, as reducing agents in organic synthesis. Synthetic strategies, structural diversity as well as some important properties and reactivities of these anhydrous metal (including scandium and yttrium) halide complexes are reviewed here. These complexes also hold potential as starting materials for constructing more sophisticated heterometallic assemblies by crystal engineering; the compounds of this class, either discrete ion-pairs or coordination polymers, being discussed separately under the heading *heterometallic lanthanide and actinide halide complexes*. The aim of this article is to provide a reference text for the researchers working in the lanthanide and actinide coordination chemistry field and to identify and signify the area of future research.

Keywords: Anhydrous lanthanide halides; Actinides; Donor ligands; Coordination compounds; Heterometallic complexes; Structures

1. Introduction and scope of the review

Lanthanide complexes have been of considerable interest in the recent years as a result of their implications in optical imaging of cells, as luminescent chemosensors for medical diagnostics, contrast reagents for medical magnetic resonance imaging, shift reagents for NMR spectroscopy as well as their increasing utility in organic synthesis, bioorganic chemistry and homogeneous catalysis [1,2]. Anhydrous lanthanide and actinide halides are the most frequently and conveniently used starting materials for the synthesis of these complexes [3]. The coordination chemistry of lanthanide and actinide halides with neutral O- and/or N-donor ligands has advanced tremendously during past two decades [4–9], one important contributing factor in this development being the fact that steric factors can be optimized not only with the ligand set but also, thanks to well-known ‘lanthanide contraction’, by choosing the best metal size from the lanthanide series [10]. The choice of neutral O- or N-donor ligands for these metal halides stems from the fact that (i) a rational access to extended polynuclear lanthanide-containing assemblies with predictable and controlled geometries can be achieved using neutral macrocyclic ligands such as cryptates, crown ethers and analogous open-chain polyethylene glycols, etc. [11,12], (ii) coordination of these donor ligands can facilitate the separation of trivalent actinide (specially Am and Cm) from the trivalent lanthanides in nuclear wastes since the slightly less hard actinide ions have better affinity toward nitrogen donor ligands and form bonds with partially covalent character [8,9], (iii) lanthanide(II) halide complexes with tetrahydrofuran (thf), hexamethylphosphoramide (hmpa) or dimethoxyethane (dme) are excellent reductive and coupling reagents, which may be used under a variety of conditions to accomplish a wide range of transformations [13–15], (iv) mono- or dinuclear lanthanide halide complexes with donor ligands such as thf, Pr^iOH, py or dme are far better starting materials [16] than base-free lanthanide trihalides, which are polymeric and hence less soluble and reactive [6], and (v) many of these coordination compounds define the first step of the lanthanide halide based catalytic reactions in organic chemistry [17].

The above studies have led to an exciting development of homometallic lanthanide and actinide halide coordination chemistry with neutral donor ligands including the recent discovery of new divalent lanthanides (neodymium, dysprosium and thulium), which are mostly iodide adducts with thf and/or dme ligands [10,18]. In addition, the concomitant stimulation of lanthanide coordination chemistry by supramolecular theme opens new perspectives for the preparation of heterometallic lanthanide halide complexes exhibiting novel properties and functions *via* intermetallic interactions [1,2]. Despite of these impressive advancements, no comprehensive attempt has been made to review the synthetic and structural aspects of this synthetically important class of compounds. This review gathers and discusses anhydrous scandium, yttrium, lanthanide and actinide halide complexes with neutral oxygen and nitrogen donor ligands (shown in Schemes 1 and 2), with a particular emphasis given to their synthetic strategies in non-aqueous media and structural variations.

2. Synthesis

Several synthetic routes to lanthanide and actinide halide complexes with O- or N-donor ligands have been reported using zero-valent metals, metal oxides or carbonates as starting reactants. These are summarized in the following pages.

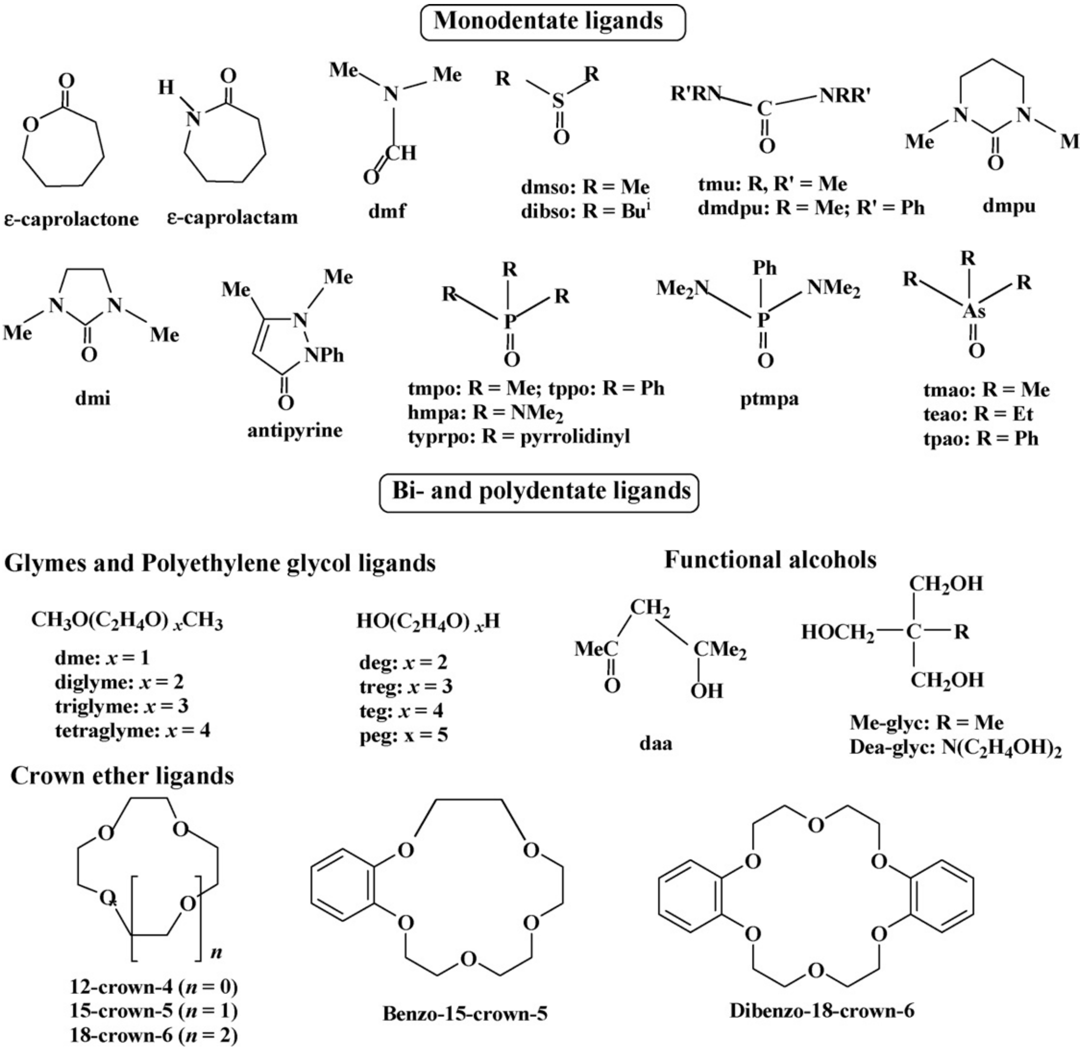
2.1. Homometallic complexes

2.1.1. Scandium, yttrium and lanthanide halide complexes

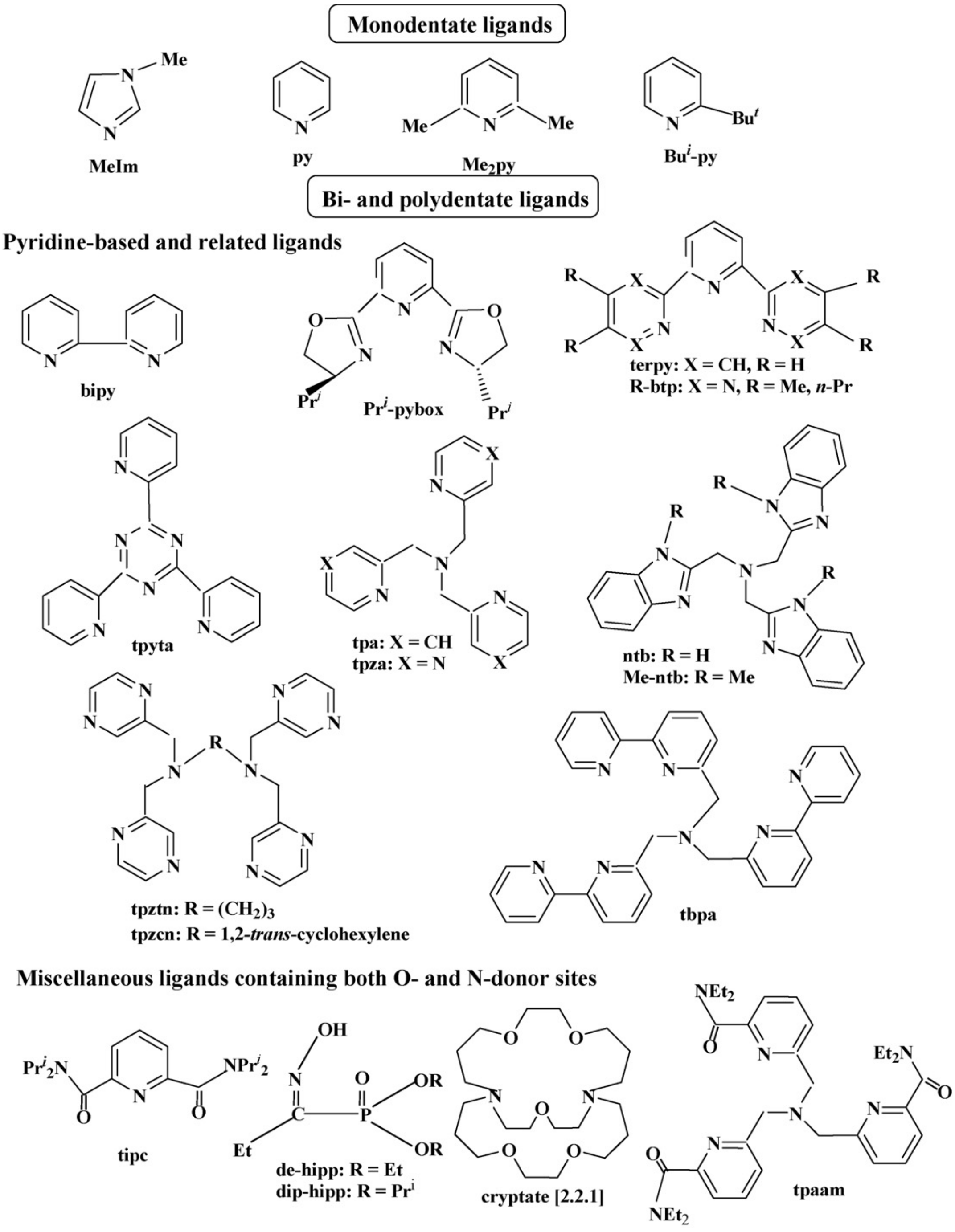
2.1.1.1. From metals. The lanthanide metals have been oxidized to the divalent state either by 1,2-diiodoethane [19–23] or molecular iodine [25,26] in the presence of thf, dme and/or higher glymes (Scheme 3). 1,2-Dibromoethane, however, fails to oxidize lanthanide metals to give lanthanide dibromide [24]. Tetrahydrofuran and dimethoxyethane adducts of some divalent lanthanide iodides (Ln = Nd, Tm) have also been prepared by heating metal powder and iodine in an evacuated glass tube followed by extraction of the powder formed with a solvent in an ultrasonic bath [25,26]. When treated with ultrasound, the reaction of samarium metal with *N*-iodine-triphenylphosphaneimine in dimethoxyethane (dme) led to two samarium complexes $[SmI_2(dme)_3]$ and $[Sm_2I(NPPh_3)_5(dme)]$, which were separated from each other by fractional crystallization [27].

A variety of lanthanide trihalide complexes have been prepared by the reactions of lanthanide metals with mercuric halide [28,29], dihaloalkane or alkyl halide (CH_2X_2, $C_2H_4X_2$, C_2H_5X; X = Br, I) [30,31], hexachloroethane [30,32,33], trimethylsilylchloride [34], gaseous hydrogen halides [35], ammonium halide [36–39] or molecular halogen (Br_2 or I_2) [40–43] in the presence of tetrahydrofuran, alcohol, dimethoxyethane or other glymes (Scheme 4).

2.1.1.2. From metal oxides and carbonates. The preparation of lanthanide halide complexes frequently involves use of the oxides (or carbonates), which are treated with some halogen containing reagents such as hydrogen halides, ammonium chloride or carbon tetrachloride [44,45]. The water is a byproduct when hydrogen halide is used, making it difficult to prepare completely anhydrous lanthanide halides [46]. Improved methods involve preparation of hydrogen chloride in situ by reacting metal oxides or carbonates with either thionyl chloride [46] or halotrimethyl-



Scheme 1. The O-donor ligands that are the subject of this review.

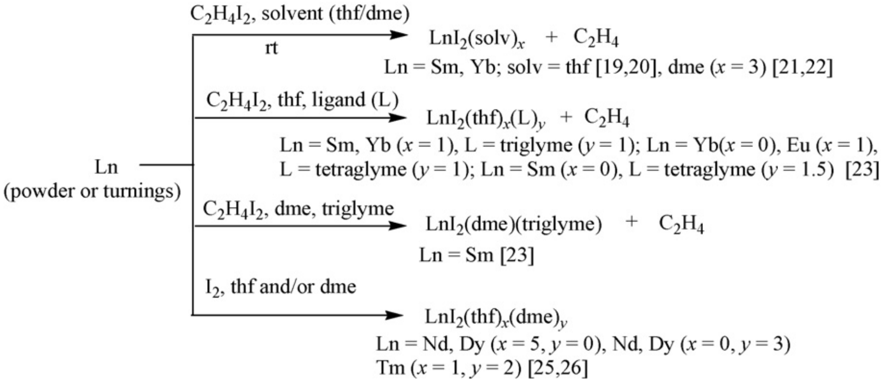


Scheme 2. The N-donor/N,O-donor ligands that are the subject of this review.

silane [16,47–49] in the presence of water (Scheme 5). The last two methods are very simple and efficient since the syntheses are carried out at rt and the side products like HCl, $(CH_3)_3SiOSi(CH_3)_3$, SO_2 and CO_2 (in the case of carbonates) are volatile and easily removed.

2.1.1.3. From metal halides/metal halide complexes and donor ligands. Removal of water from the hydrate $LnCl_3(H_2O)_6$ using thionyl chloride in the presence of excess of solvent (thf, dme) is the usual method [46,50–52], though sometimes the product is not completely anhydrous. Dissolution of anhydrous lanthanide halides or their thf/py complexes in a donor solvent (or a mixture of them) and subsequent crystallization is also widely used [53–61].

2.1.1.4. Miscellaneous methods. Using lithium dispersion in thf, Kagan et al. reported the reduction of $SmBr_3$ (prepared from Sm_2O_3) into $SmBr_2(thf)_x$ [24]. The LiBr formed is more soluble in thf and, therefore, can easily be separated from the partially soluble $SmBr_2(thf)_x$ by decantation of the mother



Scheme 3. Synthesis of lanthanide(II) halide complexes with neutral O- and/or N-donor ligands from metal powders.

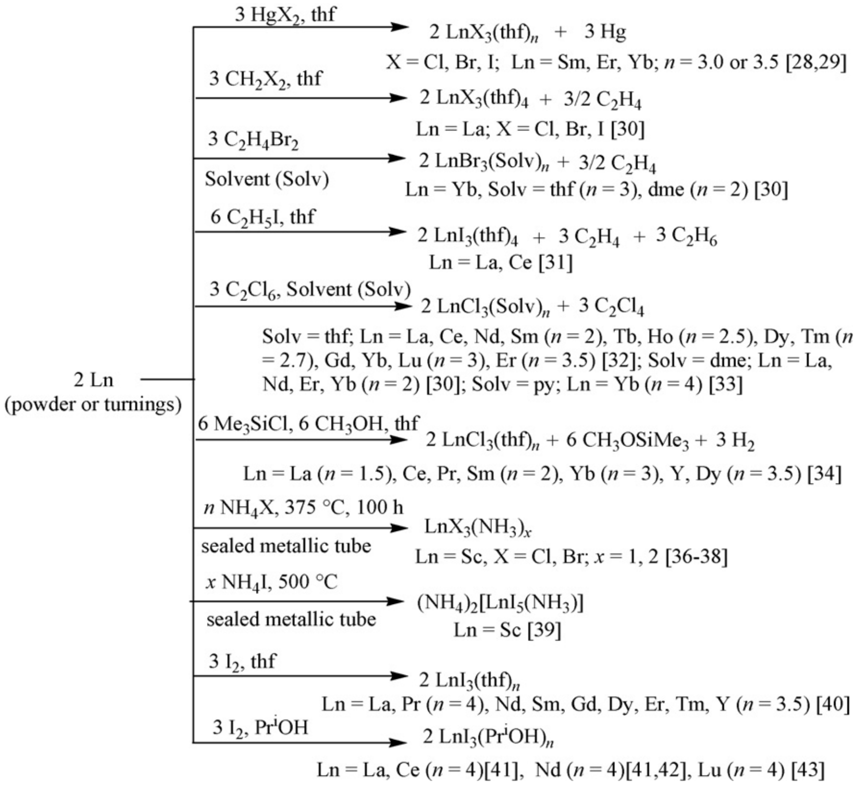
solution, followed by washing with thf. $EuI_2(thf)_5$ [62] and $YbI_2(thf)_4$ [63] were prepared as a redistributed product of the heteroleptic monoiodo derivatives $Eu(C_6H_3Ph_2\text{-}2,6)I(thf)_x$ and $Yb(OC_6H_2Bu^t\text{-}2,6\text{-}Me\text{-}4)I(thf)_x$, respectively, which undergo Schlenk-type of redistributions as shown in Eq. (1). As a breakthrough synthesis of highly reactive 'new' divalent lanthanide complexes, thulium(II) iodide complex $[TmI_2(\eta^2\text{-dme})_2(\eta^1\text{-dme})]$ was synthesized by the reaction of TmI_3 and Tm in the presence of dme [64]. Oxidation of samarium(II) diiodide by O_2 gives $[SmI_2(thf)_5][SmI_4(thf)_2]$ [65]. An ytterbium(III) iodide, $[YbI_2(thf)_5][YbI_4(thf)_2]$ has also been isolated from the reaction between an organoytterbium(II) complex and neopentyl iodide [66]. Two lanthanide halide complexes, $[NdCl_3(dme)_2]_2$ and $[YbCl_2(thf)_5][YbCl_4(thf)_2]$ have been isolated in high yield from attempts to prepare $[LnCl_{3-x}(L)_n][AlCl_4]_x$ (L = thf or dme, $x = 1\text{–}3$, $n = 3, 5$) complexes [67].

$$\mathrm{LnI(L)(thf)}_x \xrightarrow{\text{thf}} \mathrm{LnI_2(thf)}_y + \mathrm{Ln(L)_2(thf)}_z \qquad (1)$$

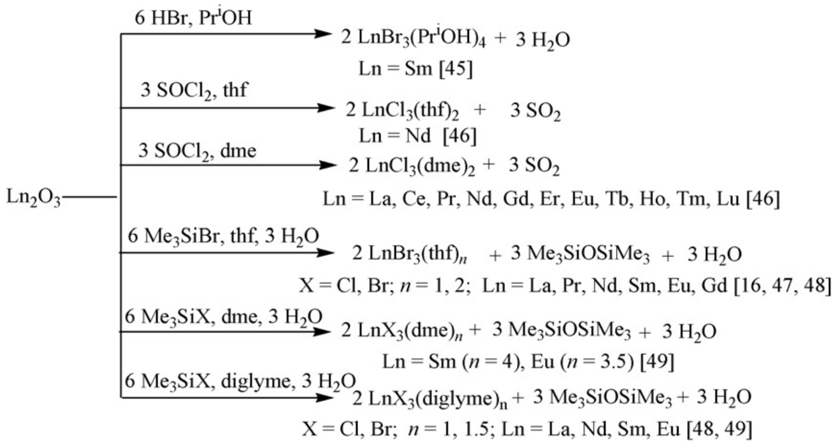
where Ln = Eu, L = $C_6H_3Ph_2$-2,6, $y = 5$, $z = 2$ [62] and Ln = Yb, L = $OC_6H_2Bu^t$-2,6-Me-4, $y = 4$, $z = 3$ [63].

2.1.2. *Actinide halide complexes*

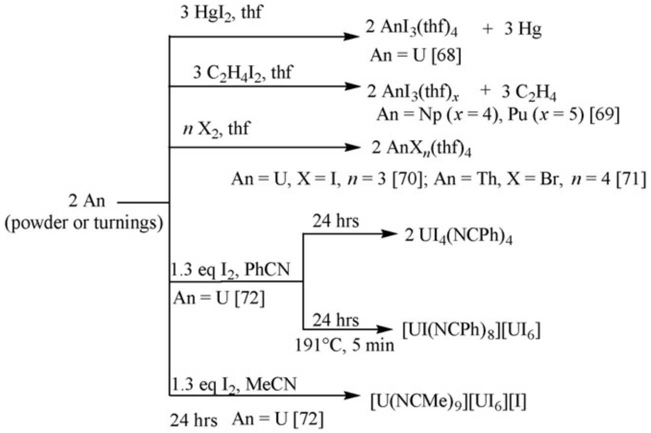
Like lanthanide metals, the actinide metals have also been oxidized in the presence of tetrahydrofuran by mercuric halide [68], diiodoethane [69] or molecular halogen (Br_2 or I_2) [70,71] to give thf-complexed tri- or tetrahalides (Scheme 6). The reaction of oxide-free uranium turnings with molecular iodine in acetonitrile or benzonitrile gives U(IV) or mixed U(III)/U(IV) complexes depending upon reaction conditions and nature of



Scheme 4. Synthesis of lanthanide(III) halide complexes with neutral O- and/or N-donor ligands from metal powders.



Scheme 5. Synthesis of lanthanide halide complexes with neutral O- and/or N-donor ligands from metal oxides (reaction sequence for $Ln_2(CO_3)_3$ is similar, except that carbon dioxide is also produced).



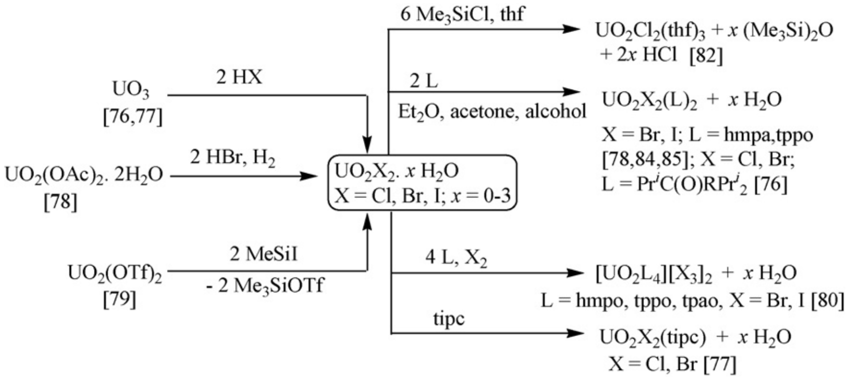
Scheme 6. Synthesis of actinide halide complexes with neutral O- and/or N-donor ligands from metal powders.

the nitrile used [72] (Scheme 6). Unlike lanthanides, direct oxidation of uranium and thorium with iodine in isopropanol leads to the isolation of mixed iodide–alkoxide complexes $[An_2I_4(OPr^i)_4(HOPr^i)_2]$ (An = Th [40], U [73]) instead of the expected *tetrakis*-isopropanol adducts of actinide iodides. Direct electrochemical oxidation of thorium disks by molecular chlorine or bromine in acetonitrile has also been reported for $ThX_4(NCMe)_4$ compounds (X = Cl, Br) [74]. Reaction of UCl_4 and excess of Me_3SiI in acetonitrile provides a convenient route to $[UI_4(MeCN)_4]$ and $[UI_2(MeCN)_7][UI_6]$ [75]. The hydrate uranyl halide complexes $UO_2X_2{\cdot}xH_2O$ (X = Cl, Br, I), which can conveniently be prepared from UO_3 [76,77], $UO_2(OAc)_2{\cdot}2H_2O$ [78] or $UO_2(OTf)_2$ [79], have proved to be excellent precursors for the development of uranyl(V) and –(VI) chemistry (Scheme 7). The hydrocarbon-soluble uranyl halide-thf complexes $[UO_2Cl_2(thf)_2]_2$ [81] and $[UO_2X_2(thf)_3]$ X = Cl, Br, I [79,82,83] are also very useful starting materials for the synthesis of anhydrous uranyl halide complexes with neutal O- and N-donor ligands [86,87].

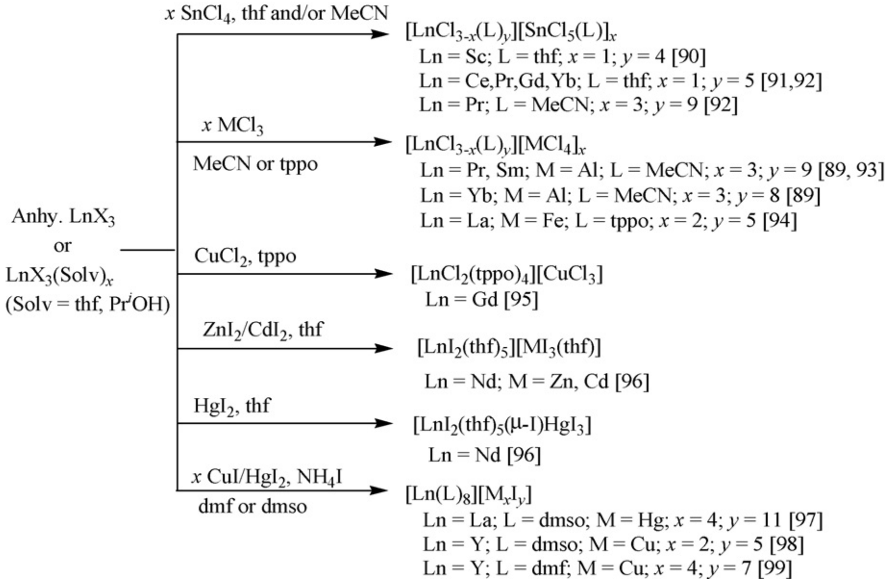
Recently, synthesis of imido analogs of the uranyl complex $[UO_2I_2(thf)_3]$ has been reported using either uranium turnings or $UI_3(thf)_4$, corresponding amines and molecular iodine as starting reagents [88].

$$U + 6Bu^tNH_2 + 3I_2 \xrightarrow{thf} [UI_2(=NBu^t)_2(thf)_2] + 4Bu^tNH_3I \tag{2}$$

$$UI_3(thf)_4 + 2PhNH_2 + \frac{3}{2}I_2 \xrightarrow{Et_3N,thf} [UI_2(=NPh)_2(thf)_3] + 4NEt_3HI \tag{3}$$



Scheme 7. Synthesis of uranyl halide complexes with neutral O- and/or N-donor ligands from hydrate uranyl halide compounds.



Scheme 8. Synthesis of heterometallic lanthanide(actinide) halide complexes with neutral O- and/or N-donor ligands.

2.2. *Heterometal lanthanide and actinide halide complexes*

The preparation of $[Ln(MeCN)_9][AsF_6]_3 \cdot xMeCN$ (Ln = La, Sm) takes advantage of the lability of the SO_2 and AsF_6 ligands of the $[\{Ln(OSO)_n(AsF_6)_3\}_x]$ complexes with displacement of SO_2 and splitting of the Ln–F–As–F–Ln bridges at rt [89].

$$[\{Ln(OSO)_n(AsF_6)_3\}_x] + \underset{\text{in excess}}{MeCN} \rightarrow x[Ln(MeCN)_9][AsF_6]_3 \cdot yMeCN + SO_2$$

$$Ln = La(y = 1), Sm(y = 3) \qquad (4)$$

The solvated lanthanide halides $LX_3(solv)_x$ (solv = thf, Pr^iOH) react with other main group or transition metal halides MX_n (M = Al, Sn, Sb, Fe, Cu, Zn, Cd, Hg; X = Cl, I; n = 1–4) to form heterometal compounds with total or partial transfer of halides from Ln to M [89–99] (Scheme 8). Alternatively, some of these complexes can also be prepared conveniently in a one-pot reaction between a lanthanide metal, C_2Cl_6 and MCl_3 in acetonitrile under ultrasonication [89]. Very recently, a uranyl(V)-alkali metal heterometallic $\{[UO_2(py)_5][KI_2(py)_2]\}_\infty$ has been prepared by the reaction of $UO_2I_2(thf)_3$ with one equivalent of KC_5R_5 (R = H, Me) in pyridine [100].

The above ionic species are attractive precursors to anhydrous hetrometallic macrocyclic complexes by direct ligand exchange of the loosely bound thf or acetonitrile ligands of the cation with crown ether ligands [101–107]. Addition of 15-crown-5 to $[GdF(AsF_6)_2]$, both dissolved in liquid SO_2, followed by crystallization at −30 °C leads to the isolation of an interesting tetranuclear ionic complex $[Gd_4F_7(15\text{-crown-}5)_4][AsF_6]_5 \cdot 6SO_2$ which is stable up to −10 °C [108].

3. Structural diversity

The structural variety of lanthanide and actinide halide complexes depends on size and coordination mode of halide and neutral ligands. A transition from one to another type of structure could be associated to a change of coordination number because of lanthanide contraction and/or coordination mode of halide, which is either a terminal or bridging one. A decrease of coordination number and associated transition to another structural type appears at lighter lanthanides, some lanthanides even form two or three different types of complexes with a same ligand, and therefore simultaneously revealing transitions to lower coordination numbers [6,16].

3.1. *Lanthanide(II) halide complexes*

Until a decade ago, the chemistry of Ln(II) compounds was confined to the complexes of traditional Sm, Eu and Yb only, whose redox potentials are readily accessible under normal solution conditions. Moreover, these three lanthanides have convenient synthetic precursors in the form of hydrocarbon-soluble $LnI_2(thf)_x$, which allow their chemistry to be explored. However, in the last few years, complexes of other divalent lanthanides namely neodymium, dysprosium and thulium have been successfully characterized mainly by Prof. Evans and Prof. Bochkarev's groups [10,18], among which thulium(II) derivatives are the most studied ones. The fact that most of presently known molecular compounds of divalent neodymium, dysprosium, and thulium are diiodide complexes, which usually contain thf and/or dme molecules as coordinated ligands, underlines the importance of these ligands in Ln(II) chemistry. These are also useful starting reagents for various organic and organometallic syntheses. Attempts to synthesize the complexes with other ligands, such as NH_3, py, MeCN, and PhCN have proved unsuccessful so far because of easy oxidation of the active bivalent metal with these compounds.

3.1.1. *Complexes with oxygen donor ligands*

3.1.1.1. Monodentate ligands. Tetrahydrofuran complexes. The coordination chemistry of Ln(II) halides with monoden-

Table 1
X-Ray crystallographically characterized complexes of anhydrous Ln(II) halides with neutral O- and N-donor ligands

S. No.	Compound	Coordination environment and geometry	Crystal system and space group	Selected bond lengths (Å)	
				Ln–X	Ln–O
Oxygen donor ligands					
1	*trans*-[LnI$_2$(thf)$_5$] Ln = Nd (**1**) [27], Sm (**2**)[a] [109], Eu (**3**) [62]	O$_5$I$_2$, pb	Monoclinic, $P2_1/n$	(**1**): 3.256(1)–3.291(1) (**3**): 3.228(2)–3.239(2)	(**1**): 2.584(8)–2.629(8) (**3**): 2.560(1)–2.653(2)
2	*trans*-[YbI$_2$(thf)$_4$] (**4**) [63]	O$_4$I$_2$, Oh	Monoclinic, $P2_1/c$	3.103(1)	2.373(8)–2.399(9)
3	*trans*-[SmI$_2$(hmpa)$_4$] (**5**) [110,111]	O$_4$I$_2$, Oh	Monoclinic, $P2_1/n$	3.390(2)	2.444(5)–2.515(6)
4	[Sm(hmpa)$_6$]I$_2$ (**6**) [111]	O$_6$, Oh	Orthorhombic, $Aba2$	–	2.447(1)–2.566(1)
5	*trans*-[Yb(hmpa)$_4$(thf)$_2$]I$_2$ (**7**) [110,111]	O$_6$, Oh	Orthorhombic, $Ibca$	–	2.454(1)–2.470(1) (thf) 2.347(6)–2.366(6) (hmpa)
6	*trans*-[SmI$_2$(tmu)$_2$(thf)$_2$] (**8**) [112]	O$_4$I$_2$, Oh	Triclinic, $P1$	3.312(2)–3.317(9)	2.436(7)–2.458(8) (tmu) 2.509(9)–2.541(8) (thf)
7	*trans*-[SmI$_2$(L)$_4$], L = dmi (**9**), dma (**10**) [112]	O$_4$I$_2$, Oh	(**9**): monoclinic, $2/m$ (**10**): tetragonal, 4_32_12	(**9**): 3.345(9)–3.357(9) (**10**): 3.309(1)	(**9**): 2.396(6)–2.590(1) (**10**): 2.450(1)
8	[Sm(dmpu)$_6$]I$_2$ (**11**) [112]	O$_6$, distrd. ta	Trigonal, $P321$	–	2.475(7)–2.488(9)
9	*trans*-[SmI$_2$(dmpu)$_3$(thf)] (**12**)[a] [112]	O$_4$I$_2$, Oh	Monoclinic, $P2_1/n$	–	–
10	[(η^2-dme)$_2$SmBr(μ-Br)]$_2$ (**13**) [113]	O$_4$Br$_3$, distrd. pb	Triclinic, $P1$	2.994(2)–3.083(3)	Sm-O 2.597(5)–2.662(5)
11	*trans*-[LnI$_2$(η^2-dme)$_2$(thf)] Ln = Sm (**14**) [109], Tm (**15**) [25,26]	O$_5$I$_2$, pb	Monoclinic, $C2/c$	(**14**): 3.246(1) (**15**): 3.151(5)	(**14**): 2.530(5) (thf), 2.595(5)–2.640(5) (dme); (**15**): 2.438(8) (thf), 2.501(6)–2.551(6) (dme)
12	*trans*-[SmI$_2$(η^2-dme)(thf)$_3$] (**16**) [109]	O$_5$I$_2$, pb	Monoclinic, $P2_1/c$	3.231(1)–2.235(1)	2.553(4)–2.581(4) (thf) 2.636(4)–2.646(4) (dme)
13	[LnI$_2$(η^2-dme)$_3$] Ln = Sm (**17**) [21,114], Dy (**18**) [115], Eu (**19**) [116]	O$_6$I$_2$, distrd. Hb or dh	Monoclinic, $P2_1$ (or $C2/c$)	(**17**): 3.289(4)–3.383(8) (**18**): 3.237(3)–3.262(3) (**19**): 3.343(1)–3.370(1)	(**17**): 2.644(4)–2.746(9) (**18**): 2.585(2)–2.678(2) (**19**): 2.640(4)–2.668(4)
14	[LnI$_2$(η^2-dme)$_2$(η^1-dme)] Ln = Tm (**20**) [64], Yb (**21**) [22]	O$_5$I$_2$, distrd. pb	Triclinic, P-1	(**20**): 3.142(2)–3.185(2) (**21**): 3.171(9)–3.120(9)	(**20**): 2.467(2)–2.498(1) (**21**): 2.479(5)–2.505(5)
15	*trans*-[YbI$_2$(η^2-dme)$_2$]$_2$(μ-dme)] (**22**) [117]	O$_5$I$_2$, pb	Triclinic, P-1	3.158(1)–3.120(1)	2.476(4)–2.514(4)
16	*trans*-[SmI$_2$(η^3-diglyme)$_2$] (**23**) [56]	O$_6$I$_2$, distrd. hb	Monoclinic, $P2_1/n$	3.265(1)	2.676(4)–2.720(4)
17	*cis*-[SmI$_2$(η^3-diglyme)$_2$] (**24**) [57]	O$_6$I$_2$, distrd. dh	Orthorhombic, $Pbca$	3.322(1)–3.333(1)	2.653(9)–2.699(1)
18	*cis*-[SmI$_2$(η^4-triglyme)(thf)] (**25**) [23]	O$_5$I$_2$, pb	Orthorhombic, $Pna2_1$	3.207(1)–3.256(1)	2.581(1) (thf), 2.609(1)–2.653(1) (triglyme)
19	*trans*-[YbI$_2$(η^4-triglyme)(thf)] (**26**) [23]	O$_5$I$_2$, pb	Orthorhombic, $Pca2_1$	3.103(1)–3.119(1)	2.432(1) (thf), 2.508(9)– 2.525(8) (triglyme)
20	*trans*-[SmI$_2$(η^4-triglyme)(η^2-dme)] (**27**) [23]	O$_6$I$_2$, distrd. hb	Triclinic, $P1$	3.275(1)–3.304(1)	2.653(9)–2.682(9) (dme) 2.645(9)–2.743(9) (triglyme)
21	*trans*-[YbI$_2$(η^5-tetraglyme)] (**28**) [23]	O$_5$I$_2$, pb	Monoclinic, $P2_1$	3.078(1)–3.128(1)	2.367(1)–2.522(2)
22	*trans*-[EuI$_2$(η^5-tetraglyme)(thf)] (**29**) [23]	O$_6$I$_2$, distrd. hb	Orthorhombic, $Pnma$	3.226(2)–3.294(2)	2.628(1) (thf), 2.618(9)–2.656(1) (tetraglyme)
23	[Sm(η^5-tetraglyme)$_2$][SmI$_3$(η^4-tetraglyme)][I] (**30**) [23]	O$_{10}$/O$_4$I$_3$, pb (anion)	Triclinic, $P1$	3.260(2)–3.282(2) (anion)	2.667(1)–2.822(1) (cation) 2.604(1)–2.655(1) (anion)

S. No.	Compound	Coordination environment and geometry	Crystal system and space group	Selected bond lengths (Å)	
				Ln–X	Ln–N
Nitrogen donor ligands					
24	*cis*-[Sm(μ-I)$_2$(NCCMe$_3$)$_2$]$_\infty$ (**31**) [56]	I$_4$N$_2$, distrd. Oh	Hexagonal, $P3_121$	3.225(1)–3.260(1)	2.596(8)
25	*trans*-[LnI$_2$(3,5-Me$_2$py)$_4$], Ln = Sm (**32**), Yb (**33**) [58]	N$_4$I$_2$, Oh	Tetragonal, $I4$	(**32**): 3.221(1) (**33**): 3.132(1)	(**32**): 2.708(1) (**33**): 2.586(3)
26	*trans*-[YbI$_2$(Bu^t-py)$_4$] (**34**) [58]	N$_4$I$_2$, Oh	Monoclinic, $C2/c$	3.120(2)	2.552(1)–2.563(1)
27	[LnI(μ-I)(N-MeIm)$_3$]$_2$, Ln = Sm (**35**), Eu (**36**)[a] [118]	N$_3$I$_3$, Oh	Monoclinic, $P2_1/n$	3.237(1)–3.307(1)	2.621(7)–2.641(6)
28	*cis*-[EuI$_2$(Pr^{i}NH$_2$)$_4$] (**37**) [119]	N$_4$I$_2$, distrd. tb	Orthorhombic, $P2_12_12_1$	3.285(3)–3.286(3)	2.651(3)–2.697(3)
29	*trans*-[TmI$_2$(Pr^{i}NH$_2$)$_4$] (**38**) [119]	N$_4$I$_2$, distrd. tb	Monoclinic, $P2_1/c$	3.132(3)	2.532(4)–2.575(3)

Table 1 (*Continued*)

S. No.	Compound	Coordination environment and geometry	Crystal system and space group	Selected bond lengths (Å)	
				Ln–X	Ln–N/Ln–O
Oxygen and nitrogen donor ligands					
30	*trans*-[$YbI_2(HNPPh_3)(\eta^2$-dme$)_2$](**39**) [117]	NO_4I_2, distrd. pb	Monoclinic, $P2_1$	3.138(1)–3.182(1)	2.510(5) (N) 2.461(4)–2.600(5) (O)

[a] Limited quality of crystallographic data.

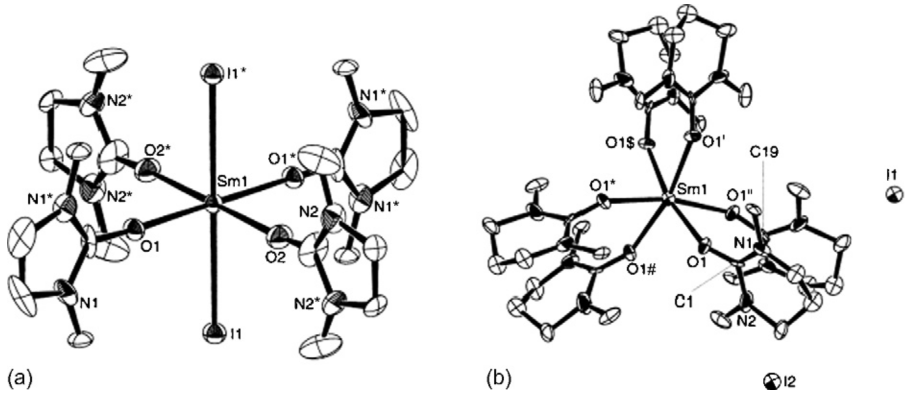


Fig. 1. Structures of (a) [$SmI_2(dmi)_4$] (**9**) and (b) [$Sm(dmpu)_6]I_2$ (**11**). Reproduced from Ref. [112] by permission of the Chemical Society of Japan.

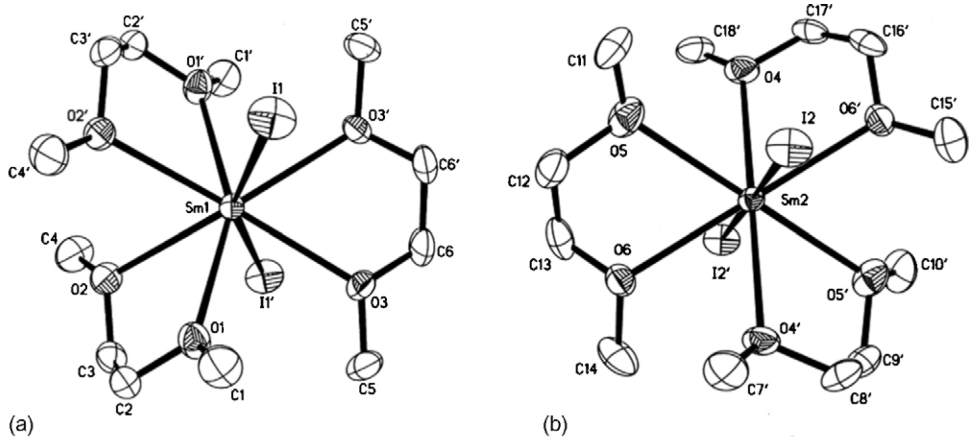
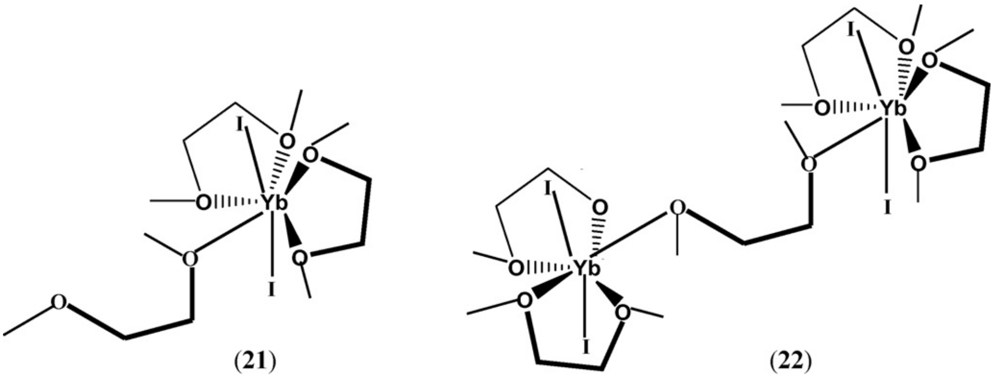


Fig. 2. Structure of [$SmI_2(\eta^2$-dme$)_3$] (**17**) showing both (a) bent, and (b) linear arrangements of iodide ligands. Reproduced from Ref. [114] by permission of the Elsevier.



(**21**) (**22**)

Fig. 3. Structures of [$YbI_2(\eta^2$-dme$)_2(\eta^1$-dme)] (**21**) and [$YbI_2(\eta^2$-dme$)_2]_2(\mu$-dme) (**22**).

tate oxygen donor ligands such as thf and hmpa has been explored to their iodides mainly, as a result of the use of LnI_2 (especially SmI_2) as standard one-electron reductants in synthetic organic chemistry. These thf derivatives are commercially available, which has allowed the chemistry of these divalent lanthanides to be explored. Two structural types of Ln(II) iodide adducts with tetrahydrofuran are known; 7-coordinated *trans*-$[LnI_2(thf)_5]$ Ln = Nd (**1**) [25,26], Sm (**2**) [109], Eu (**3**) [62] for early lanthanides and 6-coordinated *trans*-$[YbI_2(thf)_4]$ (**4**) [63] for late lanthanides (Table 1).

Hexamethylphosphoramide complexes. The addition of hmpa in the thf solution of LnI_2 not only significantly enhances the reducing power of lanthanide(II) iodide, but to some an extent, also influences the regio- and stereo-selectivity of these LnI_2-promoted reactions [110,111]. The coordination of hmpa to the LnI_2 is thought to be responsible for these effects [111]. The lanthanide(II) iodide–hmpa complexes are all mononuclear in which lanthanide centres are six-coordinated. Whether iodide is in the inner coordination sphere or not, depends on the number of hmpa as well as other solvent molecules. So unlike in *trans*-$[SmI_2(hmpa)_4]$ (**5**), where two iodide ions are part of octahedron [110,111], the $[Sm(hmpa)_6]I_2$ (**6**) [111] and *trans*-$[Yb(hmpa)_4(thf)_2]I_2$ (**7**) [110,111] have them in outer coordination sphere. A perusal of these structural data shows that (i) electron donating ability of hmpa is much stronger than that of thf, and (ii) the Sm–I bonds in hmpa-coordinated SmI_2 complexes are very weak and can easily be cleaved by a coordinating ligand. For example, average Yb–O(hmpa) and Yb–O(thf) in **7** are 2.356 and 2.462 Å, respectively, whereas the average Sm–I bond length in **5** (3.390 Å) is significantly longer than the ones found in other six-coordinate samarium(II) derivatives, e.g., 3.311 Å in $[SmI_2(tmu)_2(thf)_2]$ (**8**) [112].

Urea and amide complexes. Owing to the suspected carcinogenicity of hmpa, some urea and amide derivatives such as tmu, dmi, dma, dmpu, etc., have been employed recently as alternative additives for the reduction enhancement of SmI_2 [112]. Like hmpa, these are strong electron-donating ligands, which show significant enhancement in the reductivity of SmI_2. Coordination chemistry of SmI_2 with these ligands has been carried out in order to investigate the structure–reactivity relationships of the SmI_2 complexes generated in situ [112]. The X-ray structures of *trans*-$[SmI_2(tmu)_2(thf)_2]$ (**8**), *trans*-$[SmI_2(L)_4]$, L = dmi (**9**), dma (**10**), $[Sm(dmpu)_6]I_2$ (**11**) and *trans*-$[SmI_2(dmpu)_3(thf)]$ (**12**) show comparable structural features where the central samarium ion is six-coordinated (Fig. 1) [112]. Formation of **11** or **12** depends strictly on the relative stoichiometries of dmpu and SmI_2. In comparison to the octahedral geometries in **8**–**10**, the samarium ion in **11** has a distorted trigonal antiprismatic geometry with a large deviation in the ligand–Sm–ligand angle (O1–Sm–O1*) (76°) from 90° in an octahedral structure. The average metal–amide oxygen bonds, i.e. Sm–O(tmu) [2.446(8) Å] in **8**, Sm–O(dmi) [2.480(1) Å] in **9**, Sm–O(dma) [2.465(9) Å] in **10**, and Sm–O(dmpu) [2.482(9) Å] in **11** are much shorter than the Sm–O(thf) bonds in $[SmI_2(dme)_2(thf)]$ (**14**) [2.530(5) Å] and $[SmI_2(dme)(thf)_3]$ (**16**) [2.571(4) Å], though compounds **14** and **16** have seven-coordinate samarium centres [109]. These bond lengths are either same or slightly shorter than Sm–O(hmpa) bonds in **5** [av. 2.50(6) Å] and **6** [av. 2.53(1) Å]. These comparisons clearly indicate that these amides are strong donor ligands. Elongation of the Sm–I bonds was also observed due to the strong coordination of amide ligands. The average Sm–I bond distances in complexes **8** [3.312(1) Å], **9** [3.351(9) Å] and **10** [3.310(1) Å] are slightly shorter than that in **5** [3.390(2) Å], but they are longer than those present in other diiodosamarium complexes such as in **14** [3.246(1) Å] and **16** [3.233(1) Å] [109].

3.1.1.2. Potential bi- and polydentate ligands. Glyme complexes. The dme or mixed thf–dme adducts of LnX_2 (X = Br, I) show interesting but definite pattern of structures. The only bromide complex $[(\eta^2\text{-dme})_2SmBr(\mu\text{-Br})]_2$ (**13**) is a 7-coordinate bromide-bridged dimer [113]. Mixed dme–thf complexes $[LnI_2(\eta^2\text{-dme})_2(thf)]$ (Ln = Sm (**14**) [109], Tm (**15**) [25,26]) and $[SmI_2(\eta^2\text{-dme})(thf)_3]$ (**16**) [109] are also 7-coordinate, though they are monomeric. The potential bidentate dme can also act as a monodentate ligand depending upon steric consideration around metal centre. So unlike larger lanthanides, which have all three dme acting as bidentate ligands in 8-coordinate $[LnI_2(\eta^2\text{-dme})_3]$ (Sm (**17**) [21,114], Dy (**18**) [115], Eu (**19**) [116]), smaller lanthanides form 7-coordinate $[LnI_2(\eta^2\text{-dme})_2(\eta^1\text{-dme})]$ (Ln = Tm (**20**) [64], Yb (**21**) [22]) with two bidentate and a monodentate dme ligands. It is noteworthy that **17** can crystallize as either an enantiomer (Λ or Δ) or as a racemic mixture, depending on crystallization conditions [21]. In the structures of both **17** [114] and **18** [115], there are two independent molecules in the unit cell, one of which has a linear I–Ln–I component [180.0(9)°] and the other has a bent I–Ln–I moiety [157.3(1)–157.6(2)°] (Fig. 2). On the contrary, the compound **19** has only a bent arrangement of iodide ions [I–Eu–I = 158.5(1)°]. Interestingly, the ytterbium also forms a dme-bridged dimer, $[YbI_2(\eta^2\text{-dme})_2]_2(\mu\text{-dme})$ (**22**) [117], the formation of which can be considered as a logical consequence of a non-coordinated oxygen atom of η^1-dme ligand in **21** (Fig. 3).

Both *trans*-$LnI_2(\eta^3\text{-diglyme})_2$ (**23**) [56] and *cis*-$LnI_2(\eta^3\text{-diglyme})_2$ (**24**) [57] complexes have been reported for Sm(II), in which 8-coordinated samarium atoms have distorted hexagonal bipyramidal and dodecahedral geometries, respectively. The average Sm–I distance, 3.328 Å, in the *cis* isomer **24** is significantly longer than the one found in the *trans* isomer **23** (3.265 Å) [56,57]. It is also interesting to note that while $[SmI_2(\eta^4\text{-trigly})(thf)]$ (**25**) [23] has the iodide ligands in a *cisoid* arrangement, the ytterbium analogue is isolated as *trans*-$[YbI_2(\eta^4\text{-trigly})(thf)]$ (**26**) [23], probably due to the smaller size of ytterbium ion. On replacing the thf ligand in **25** by a dme ligand, eight-coordinate *trans*-$[SmI_2(\eta^4\text{-trigly})(\eta^2\text{-dme})]$ (**27**) is obtained, which crystallizes as two enantiomers. The iodide ligands are in *trans* positions and the coordination geometry is a distorted hexagonal bipyramid, although the dme ligand is tilted with respect to the equatorial plane [23]. All three triglyme complexes **25**–**27** are chiral in the solid state, since the triglyme ligand forms an odd number (three) of five membered rings upon coordination to the metal. Due to the presence of sterically

Table 2
Comparison of ionic radii (Å) of alkaline earth metals and divalent lanthanide metals

Coordination number	Ionic radii of alkaline earth metal cations			Ionic radii of divalent lanthanide cations		
	Ca^{2+}	Sr^{2+}	Ba^{2+}	Yb^{2+}	Eu^{2+}	Sm^{2+}
6	1.00	1.18	1.35	1.02	1.17	–
7	1.06	1.21	1.38	1.08	1.20	1.22
8	1.12	1.26	1.42	1.14	1.25	1.27

crowded tetraglyme ligand, the thf ligand in eight-coordinate *trans*-[EuI_2(η^5-tetragly)(thf)] (**28**) remains distinctly out of the equatorial plane resulting in bending of the I–Eu–I axis, whereas the smaller ytterbium(II) crystallizes without any thf ligand as *trans*-[YbI_2(η^5-tetraglyme)] (**29**) [23]. The remarkable structure of ion-pair [Sm(η^5-tetragly)$_2$][SmI_3(η^4-tetragly)][I] (**30**) has a 10-coordinate cationic complex and two anions, a seven-coordinate [SmI_3(tetragly)]$^-$ and a iodide ion, to balance the charge [23].

3.1.2. Complexes with nitrogen donor ligands

Only few structurally characterized lanthanide(II) iodide complexes with neutral N-donor ligands are known [56,58,118,119] and they, regardless of their ionic radii, have been shown to prefer a six-coordinate environment around central metal. The geometry around each samarium in [Sm(μ-I)$_2$($NCCMe_3$)$_2$]$_\infty$ (**31**) [56] is thus a distorted octahedral, the ligating atoms being the two nitrogen atoms and the four bridging iodide ions. All iodide are bridging, resulting in infinite chains of repeating unit $SmI_2(NCCMe_3)_2$. The two-nitrile ligands have a *cis* configuration and the Sm–N=C angle is 151.3(6)°. The three X-ray crystallographically characterized Ln(II) iodide complexes with substituted pyridines, [LnI_2(3,5-Me_2py)$_4$] [Sm (**32**), Yb (**33**)] and [YbI_2(Bu^t-py)$_4$] (**34**) are also six-coordinate with iodide ions in *trans* positions [58]. The compounds [LnI(μ-I)(N-MeIm)$_3$]$_2$, Ln = Sm (**35**), Eu (**36**) [118] are dimer in which each metal atom exhibits an octahedral coordination environment composed of one terminal and two bridging iodide ligands and three terminal N-MeIm ligands. The three-iodide ions and the three imidazole ligands around each samarium are arranged in a meridional fashion. In comparison to other 6-coordinated iodo-bridged samarium(II) derivative **31** [56], where all of the iodide ions are bridged to give a polymer, only half of the iodide ions in **35** and **36** are in bridging position to generate a dimer. As expected, the bridging Sm–I bond distances, 3.280(1) and 3.307(1) Å, in **35** are longer than the terminal Sm–I distance, 3.237(1) Å. Interestingly, this terminal distance is equivalent to the bridging distance in **31**. The geometries of the structures of $LnI_2(Pr^iNH_2)_4$ [Ln = Eu (**37**), Tm (**38**)] can be described as distorted tetragonal bipyramid [119]. In the structure of **37** the apical positions are occupied by the I^- ion and the N atom (*trans* N–Eu–I angle 169.0°), whereas in **38** these positions are occupied by the I^- ions (*trans* I–Tm–I 180.0°). The average Eu–I bond length 3.2850 Å is somewhat longer than the same distances in the 7-coordinate **3** (3.230 Å) [62] but shorter than in the 8-coordinate **19** (3.357 Å) [116]. The average Eu–N contacts, 2.674 Å is noticeably longer than the same Eu–N bond distance in the dimer **36** (2.602 Å) [118], indicating a weaker Eu···N interaction in the **37**.

3.1.3. Comparison of divalent lanthanide iodide complexes with alkaline earth metal iodide adducts

The chemistry of some of above described lanthanide(II) compounds can be compared with those of alkaline earth metal iodide adducts with O-donor ligands because of close similarities in the size/charge ratio for Yb^{2+}/Ca^{2+} and $Eu^{2+}(Sm^{2+})/Sr^{2+}$ (Table 2). The structures of the thf-derivatives of the alkaline earth metals MI_2 (M = Ca, Sr, Ba) [120] as well as the divalent lanthanides SmI_2 [109] and EuI_2 [62] show a very close similaritiy both in terms of synthetic procedures and structural features. So the structures of both [CaI_2(thf)$_4$] [120] and [YbI_2(thf)$_4$] [63] present a square bipyramidal arrangement around the calcium/ytterbium metals with iodide atoms in axial positions, whereas due to larger ionic radii, [MI_2(thf)$_5$] (M = Sr, Ba) [120] and [LnI_2(thf)$_5$] (Ln = Sm [109], Eu [62]) accept one more thf molecule in the coordination sphere, resulting in a pentagonal bipyramidal geometry around the metal centres. The structure of *trans*-[SmI_2(hmpa)$_4$] [110,111] is strikingly similar to that of [SrI_2(hmpa)$_4$] [121a], whereas with three chelating equatorial dme ligands and two iodide ligands in apical positions of a distorted hexagonal bipyramid, the complex *trans*-[SrI_2(η^2-dme)$_3$] [121b] possesses a structure, which is an analogue to those of **17–19** [21,114–116]. As mentioned in above section, however, different chiral structures can be obtained for Sm(II) derivative **17** as a function of crystallization conditions [21,114]. Unlike divalent ytterbium Yb^{2+}, which accepts two iodide anions, two bidentate dme and one monodentate dme in monomeric **21** [22] and dimeric **22** [117], the Ca^{2+} ion in [CaI(η^2-dme)$_3$]I [122] accommodates three bidentate dme and one iodide ligands in its coordination sphere, thus maintaining heptacoordination around central metal. Although the Ba^{2+} cation is larger than Sm^{2+} (Table 2), the structural chemistry of their iodide adducts with bi- and polydentate O-donor ligands resemble each other in many cases. For example, structure of *trans*-[SmI_2(η^4-triglyme)(η^2-dme)] (**27**), which crystallizes as two independent molecules (enantiomers) per asymmetric unit [23], can be related to the recently reported *trans*-[BaI_2(η^4-triglyme)(η^2-dme)] [123]. In both compounds chirality stems from the presence of dme and triglyme ligands, which form odd numbers of five-membered rings upon coordination to the central Sm or Ba metals. Another striking structural similarity is observed in the cationic species of [M(η^5-tetraglyme)$_2$]$^{2+}$ (M = Sm, Ba) of **30** [23] and [Ba(η^5-tetraglyme)$_2$]$I_2 \cdot C_6H_7$ [123], where two tetraglyme ligands wrap

Table 3
Comparison of alkaline earth metal and divalent lanthanide iodide adducts

Metal iodide adduct	Alkaline earth metal iodide adduct					Divalent lanthanide iodide adduct				
	M^{2+}	Co. no	M–I (Å)	M–O (Å)	I–M–I (°)	M^{2+}	Co. no	M–I (Å)	M–O (Å)	I–M–I (°)
trans-$[MI_2(thf)_4]$	Ca [120]	6	3.106	2.340	180	Yb [63]	6	3.103	2.386	180
$[MI_2(thf)_5]$	Sr [120]	7	3.229	2.590	176.3	Eu [62]	7	3.238	2.550	178.3
	Ba [120]	7	3.378	2.718	178.6	–	–	–	–	–
trans-$[MI_2(hmpa)_4]$	Sr [121a]	6	3.321	2.440	180	Sm [110,111]	6	3.390	2.501	180
$[MI_2(\eta^2\text{-dme})_3]$	Sr [121b]	8	3.398	2.644	158.9	Eu [116]	8	3.357	2.655	158.5
–	–	–	–	–	–	Sm [21,114]	8	3.369	2.668	158.2
cis-$[MI_2(\eta^3\text{-diglyme})_2]$	Sr [122]	8	3.325	2.673	91.5	Sm [57]	8	3.333	2.680	92.0
$[MI_2(\eta^4\text{-triglyme})(\eta^2\text{-dme})]$	Ba [123]	8	3.442	2.302	164.4	Sm [23]	8	2.278	2.691	166.3
$[M(\eta^5\text{-tetraglyme})_2]^{2+}$	Ba [123]	10	–	2.831	–	Sm [23]	10	–	2.744	–

the 10-coordinated central metal Sm or Ba in a helical fashion. Table 3 contains comparative bond length and angle data of these compounds.

3.2. Scandium(III), yttrium(III), lanthanide(III) and uranium(III) halide complexes

One of the powerful features of the lanthanide metals is that one can use their gradually changing radial size to optimize the chemistry in ways not possible for other series of metals in the periodic table. Since the 4f valence orbitals of the lanthanides have a limited radial extension compared to the size of their core orbitals, one can choose the lanthanide with the optimal radial size to accomplish a specific reaction [10]. Hence, for reactions involving trivalent lanthanides, one can optimize steric factors not only with the ligand set, as is traditionally done with all metals, but also by choosing the best metal size from 15 non-radioactive choices. These vary gradually from 1.03 Å, La^{3+} (six-coordinate radius) to 0.86 Å, Lu^{3+} with a 0.01–0.02 Å, changing from element to element. No other series of metals in the periodic table has so many chemically similar metals with such a selection of gradually changing radial sizes.

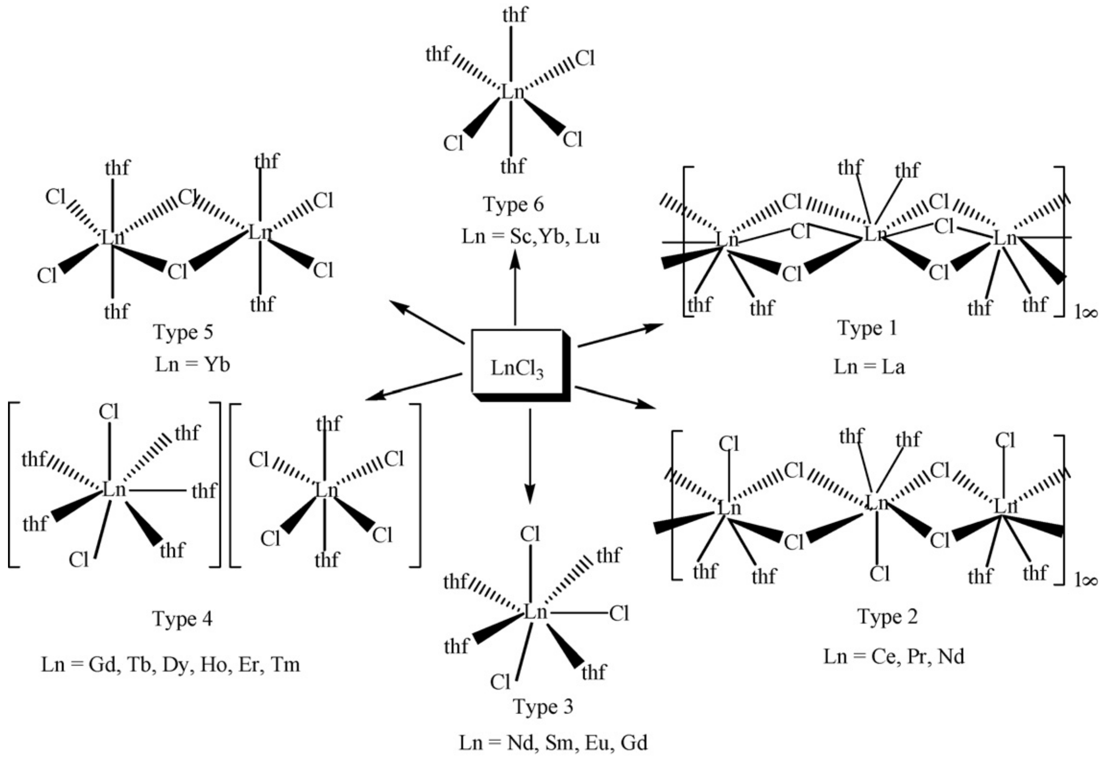
3.2.1. Complexes with oxygen donor ligands

3.2.1.1. Monodentate ligands. Tetrahydrofuran complexes. Scandium, yttrium(III) and lanthanide(III) halide complexes with tetrahydrofuran are the most commonly used starting reagents for the synthesis of their organometallic and other compounds. Lanthanide trihalide tetrahydrofuran complexes such as $NdCl_3(thf)_4$ have also been employed as Ziegler-type catalysts (in combination with trialkylaluminium reagents, R_3Al) for stereospecific polymerization of dienes [124]. A range of stoichiometries is known for lanthanide chlorides, and the formula and structures of these complexes present considerable diversity. Five different stoichiometries of $LnCl_3(thf)_x$ ($x = 2$, 2.5, 3, 3.5, 4) and six different structural types have been identified (Scheme 9). The compound obtained not only depends on the lanthanide and the reaction stoichiometry but upon reaction conditions as well [16]. The pattern across the series reflects an overall decrease in coordination number from 8 (La) to 6 (Lu). Lanthanum uniquely forms $[LaCl_3(thf)_2]$ (**40**), which has a single-stranded polymer $\cdots La(\mu\text{-}Cl)_3(thf)_2La(\mu\text{-}Cl)_3(thf)_2La\cdots$ with *cis*-thf molecules and square antiprismatic eight-coordination of lanthanum (type 1) [125]. The second type of polymeric chain $\cdots LnCl(thf)_2(\mu\text{-}Cl)_2LnCl(thf)_2(\mu\text{-}Cl)_2\cdots$ with seven-coordinate lanthanide atoms is found for Ce (**41**), Pr (**42**), Nd (**43**) and Y (**44**) [51,53,125,126]. The third type, found for Nd (**45**), Sm (**46**), Eu (**47**) and Gd (**48**), is monomeric seven coordinate $[LnCl_3(thf)_4]$ [51,124,127,128], while Gd (**49**), Tb (**50**), Dy (**51**), Er (**52**), Yb (**53**) and Y (**54**) form ion-pair structures $[LnCl_2(thf)_5]^+[LnCl_4(thf)_2]^-$ (type 4), containing a pentagonal bipyramidal cation and octahedral anion, both with *trans* geometries [51,53,113,125–127,129]. Ytterbium forms a dimeric $[Cl_2(thf)_2Yb(\mu\text{-}Cl)_2Yb(thf)_2Cl_2]$ (**55**) [32] (type 5), whilst scandium, ytterbium and lutetium form the sixth type monomeric octahedral *mer*-$[LnCl_3(thf)_3]$ [Ln = Sc (**56**), Yb (**57**), Lu (**58**)] [32,125,130,131].

In contrast to the chlorides, lanthanide bromides form only three types of thf complexes; (i) neutral 7-coordinate $[LnBr_3(thf)_4]$ [(Ln = La (**59**), Pr (**60**), Nd (**61**), Sm (**62**)] with two bromide anions in the *trans* apical positions [16,30,132], (ii) an ionic structure $[EuBr_2(thf)_5][EuBr_4(thf)_2]$ (**63**) [16], which is isostructural to type 4 of lanthanide chloride (Gd–Yb) [51,53,113,125–127,129], and (iii) a mononuclear octahedral complex *mer*-$[YbBr_3(thf)_3]$ (**64**) [30]. Lanthanide iodides form two major types of complexes with thf, seven-coordinated $[LnI_3(thf)_4]$ [Ln = La (**65**), Pr (**66**)] [40,133] for larger lanthanides, while smaller lanthanide metals auto-ionize to form the ionic complexes $[LnI_2(thf)_5][LnI_4(thf)_2]$ [Ln = Nd (**68**), Sm (**69**), Gd (**70**), Y (**71**), Yb (**72**)] [40,65,66]. Additionally, an interesting ionic structural type with an $I_3{}^-$ counterion $[LnI_2(thf)_5][I_3]$ has also been reported for La (**73**) [127] and Yb (**74**) [96]. The trivalent uranium iodide adduct $[UI_3(thf)_4]$ (**67**) [70] has a structure similar to those of **65** and **66** [40,133].

A certain trend emerges on comparing transition points of structural changes between the mononuclear and ionic structures of different halide complexes with thf in the lanthanide row, i.e., the coordination number seven extends in $[LnCl_3(thf)_4]$ from lanthanum to europium and changes to seven/six at gadolinium [125]. The same transition in analogous bromides and iodides occurs earlier in the lanthanide row, at europium [16] and neodymium [40], respectively.

Isopropanol complexes. Lanthanide halide complexes with isopropanol are among the most convenient and widely used starting materials for the synthesis of metallo-organic complexes



Scheme 9. Six different structural types of $LnCl_3(thf)_x$ ($x = 2, 2.5, 3, 3.5, 4$).

of these metals, especially metal alkoxides. The pentagonal bipyramidal geometry found in a mixed-ligand complex $[NdBr_3(thf)_2(Pr^iOH)_2]$ (**75**) [134], the dimeric $[LnCl_2(\mu\text{-}Cl)(Pr^iOH)_4]_2$ (Ln = La (**76**) [135], Ce (**77**) [136], Nd (**78**) [137]) and $SmBr_3(Pr^iOH)_4$ (**79**) [45] is considerably different from that of the capped trigonal prismatic geometry observed in the related iodide derivatives, $LnI_3(Pr^iOH)_4$ (Ln = La (**80**), Ce (**81**) [41]). A second type of structure, i.e. an auto-ionised *cis*-$[LuI_2(Pr^iOH)_4][I]$ (**82**) is also known for isopropanol complexes of Ln(III) iodides [43].

Hexamethylphosphoramide complexes. It was mentioned in Section 3.1.1 that coordination of hmpa to LnI_2 significantly enhances the reducing power of lanthanide(II) iodide. Similarly, the Ln(III) halide-hmpa/$Al(Bu^i)_3$ combination has also been shown as a novel catalytic system for copolymerization of isoprene and styrene [138]. The chemistry of Ln(III) halide complexes with hmpa ligand, either ionic [114,139,141,142] or neutral [48,140,141], is rich in six-coordinate complexes. Depending upon their synthetic routes and conditions, the six coordinate $LnCl_3(hmpa)_3$ complexes show reversible *facial–meridional* isomerism. The *mer*-$LnCl_3(hmpa)_3$ [Ln = Pr (**85**), Dy (**86**), Yb (**87**)] [140] were obtained by the reaction of $LnCl_3$ in hot ethanol, crystallized at 0 °C and then recrystallized from benzene and has one molecule per asymmetric unit, whereas the *fac*-$[LnCl_3(hmpa)_3]$ [Ln = Sm (**88**), La (**89**)] (Fig. 4) complexes were prepared by the reaction of $[LnCl_3L]$ (L = diglyme and dme) with excess hmpa at rt in toluene [48]. Except molecular $[SmBr_3(hmpa)_2(thf)]$ (**90**) [141], other 6-coordinate hmpa complexes with lanthanide(III) bromide and iodides namely $[SmBr_2(hmpa)_4]Br{\cdot}thf$ (**91**) [141], $[SmI_2(hmpa)_4]I{\cdot}2CHCl_3$ (**92**) [142] and $[TmI_2(hmpa)_4]I{\cdot}5py$ (**93**) [114] are ionic because of cleavage of one Ln–X bond. A typical octahedron consists of two halides at apical and four oxygen atoms from hmpa at equatorial positions.

Trialkyl-phosphine and -arsine oxide complexes. Phosphine oxides and related ligands have been studied in lanthanide(III) chemistry with the aim of developing selective extractants. Similar to above-mentioned hmpa complexes, the Ln(III) halide complexes with trialkyl-phosphine and -arsine oxide ligands are also six-coordinate with a regular or slightly distorted octahedral geometry [61,143–145]. Complexation of these ligands with lanthanide halide often proceed with partial or complete ionization of the halide lig-

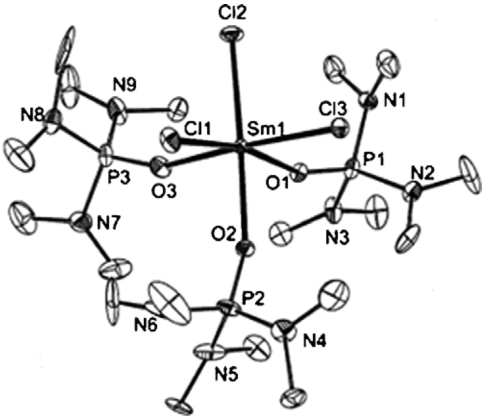


Fig. 4. Structure of *fac*-$[SmCl_3(hmpa)_3]$ (**88**). Reproduced from Ref. [48] by permission of the Elsevier.

and and except neutral *mer*-$[LnCl_3(tppo)_3]\cdot 0.5Me_2CO$ [Ln = La (**100**), Ce (**101**)] [145], other complexes namely *trans*-$[ScBr_2(tppo)_4]Br\cdot 0.5Et_2O$ (**94**) [143], $[Y(tmpo)_6]Br_3$ (**95**) [144], *trans*-$[ScCl_2(tpao)_4]Cl$ (**96**) [143], $[Sc(tmao)_6]Br_3$ (**97**) [143], *trans*-$[LnCl_2(tppo)_4]Cl\cdot x EtOH$, Ln = Tb ($x = 1.55$) (**98**), Yb ($x = 2.25$) (**99**) [145], *trans*-$[LnI_2(tppo)_4]I$, Ln = La (**102**), Ce (**103**), Nd (**104**) [61] and *trans*-$[UI_2(tppo)_4]I\cdot 3py$ (**105**) [61] are ionic. It is noteworthy that the two U–I distances are equal in **105** whereas one Ln–I bond length in the complexes **102**–**104** is ca. 0.07 Å longer than the other, suggesting that a second iodide ligand could easily be dissociated from the lanthanide triiodide upon complexation of Ph_3PO. Such a dissociation was observed in the crystallization of $[TmI_3(hmpa)_4]$ from pyridine which afforded crystals of $[TmI_2(hmpa)_4][I]\cdot 5py$ and $[TmI(hmpa)_4(py)][I]_2$ [114]. Another noteworthy point is that the U–I bond lengths are shorter than those expected from a purely ionic bonding model, by 0.04 Å. The shortening of the U–I distances with respect to the Ln–I ones in the complexes **102**–**104** can be accounted for by the softer character of the 5f versus 4f trivalent ions, leading to a stronger interaction between uranium and soft ligands.

ε-Caprolactone and ε-caprolactam complexes. Poly(ε-caprolactone) is one of the most important biocompatible/biodegradable polymers and lanthanide halides are known as very active catalysts in the ring-opening polymerization of cyclic esters [146]. To define the first step in these lanthanide-based ring opening polymerizations, the coordination chemistry of ε-caprolactone and ε-caprolactam, precursors of poly(ε-caprolactone) and nylon-6, respectively, with lanthanide trichlorides have been studied. Crystallization of a variety of lanthanide chlorides from a mixture of thf and ε-caprolactone shows that many structural variations are possible [53]. The larger neodymium and samarium form ion pairs $[Ln(\varepsilon\text{-caprolactone})_8][Cl_3Ln(\mu\text{-}Cl)_3LnCl_3]$ [Ln = Nd (**106**), Sm (**107**)] in which the cation $[Ln(\varepsilon\text{-caprolactone})_8]^{3+}$ contains a Ln^{3+} ion surrounded by eight caprolactone molecules in a square antiprismatic geometry. The anion $[Cl_3Ln(\mu\text{-}Cl)_3LnCl_3]^{3-}$ is bimetallic and contains no O-donor ligands. On the other hand, smaller yttrium and ytterbium, which differ in radius by 0.032 Å, form *mer*-$[YCl_3(\varepsilon\text{-caprolactone})_3]$ (**108**) and *fac*-$[YbCl_3(\varepsilon\text{-caprolactone})(thf)_2]$ (**109**), respectively. Though both are six-coordinated, complexes **108** and **109** differ in solubility, crystallization behavior, the amount of caprolactone incorporated, and the particular isomer formed (*fac* vs. *mer*). Surprisingly the terbium trichloride, which differs from yttrium trichloride by 0.023 Å, does not coordinate with caprolactone at all [53]. In contrast, the coordination chemistry of more basic ε-caprolactam with lanthanide trichlorides appears to be more rational and two types of cationic ε-caprolactam complexes are obtained depending on the size of the metal [54]. The larger lanthanides Ce (**110**), Pr (**111**), Nd (**112**) and Sm (**113**) form capped octahedral di-cations, $[Ln(\varepsilon\text{-caprolactam})_6Cl]^{2+}$ with the chloride ligand in the capping position (Fig. 5), whereas the smaller metals Eu (**114**), Gd (**115**) and Ho (**116**) form *trans*-octahedral monocations $[Ln(\varepsilon\text{-caprolactam})_4Cl_2]^+$. Chloride ions are the counteranions in both cases.

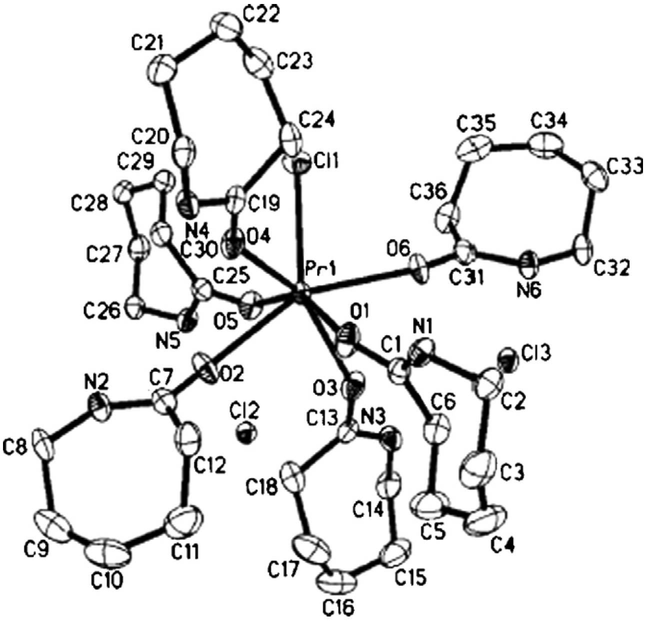


Fig. 5. Structure of $[Pr(\varepsilon\text{-caprolactam})_6Cl]Cl_2$ (**111**). Reproduced from Ref. [54] by permission of the Wiley–VCH.

Dimethyl formamide, -sulfoxide and other miscellaneous complexes. The high polar solvents such as dmf and dmso cause complete dissociation of lanthanide–halide bonds in derivatives $[Ln(dmf)_8]I_3$, Ln = Ce (**117**), Nd (**118**) [147], $[M(dmf)_9]I_3$, M = La (**119**), Ce (**120**), U (**121**) [147], $[Sc(dmso)_6]I_3$ (**122**) [148], $[Ln(dmso)_8]I_3$ Ln = Y (**123**) [149], La (**124**), Ce (**125**), Pr (**126**), Nd (**127**), Sm (**128**), Gd (**129**), Dy (**130**), Er (**131**), Lu (**132**) [150]. The 'soft nature' of iodide anions is evident in the crystal structures of **117**–**132** and other lanthanide/uranium triiodide complexes with miscellaneous ligands such as $[Sm(urea)_8]I_3$ (**134**) [152], $[Y(N,N\text{-dimethylpropylene urea})_6]I_3$ (**136**) [149] and $[Ln(antipyrine)_6]I_3$, Ln = Tb (**137**) [154], Y (**138**) [155], where iodide anions are not in the primary coordination sphere of the metal (Table S1). As described later in Section 3.4, these derivatives are potential precursors for the synthesis of some interesting heterometallic halide compounds.

3.2.1.2. Potential bi- and polydentate ligands.

Glyme complexes. Scandium(III), yttrium(III) and lanthanide(III) halide complexes with monodentate tetrahydrofuran or bidentate dimethoxyethane are the most commonly used starting reagents for the synthesis of their orgaometallic and other compounds. However, unlike for lanthanide trihalide complexes with thf, where a rich structural diversity is observed with coordination numbers varying from six to eight, only two types of structures are found for lanthanide chlorides and bromide adducts with dme; (i) binuclear $[LnX_2(\mu\text{-}X)(\eta^2\text{-dme})_2]_2$ (**141**)–(**144**) (X = Cl, Br; Ln = La, Ce, Pr, Nd [30,46,67]) and (ii) mononuclear $[LnX_3(\eta^2\text{-dme})_2]$ (**147**)–(**163**) (X = Cl, Br; Ln = Pr-Lu, Y [16,30,46,127,158–161]) (Table S1). A border between binuclear and mononuclear species is set by neodymium and praseodymium in chloride and bromide complexes, respectively [16,46,67,158]. In fact, both 8-coordinate **144** [46,67] and

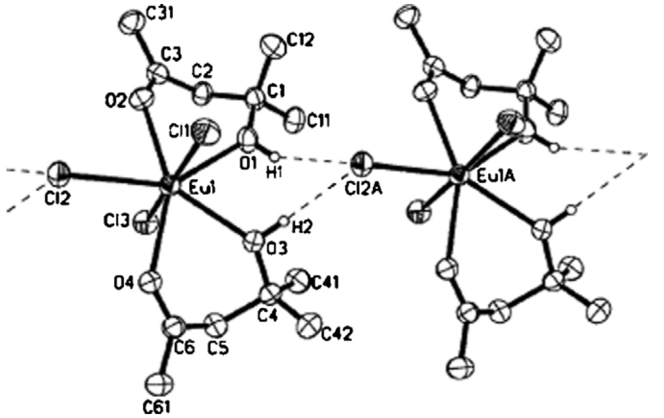


Fig. 6. Structure of $[EuCl_3(\eta^2\text{-daa})_2]$ (**169**) showing intermolecular H···Cl bonding. Reproduced from Ref. [55] by permission of the Wiley–VCH.

seven-coordinated **147** [158] forms are known for neodymium chloride.

Scandium(III) chloride forms six-coordinate molecular complex $[ScCl_3(\eta^3\text{-diglyme})]$ (**164**) with diglyme [52]. On the other hand, the ion-pair complexes $[LnBr_2(\eta^3\text{-diglyme})_2][LnBr_4(\eta^3\text{-diglyme})]$ (Ln = La (**165**) [23], Sm (**166**), Eu (**167**) [49]) have coordination numbers 8 and 7 for cation and anion, respectively. The cation has two bromide atoms in *cis* configuration. Each seven-coordinate lanthanide ion in an anion adopts a distorted pentagonal bipyramidal geometry with two bromide in axial positions and two bromide ions and three oxygen atoms from diglyme in equatorial positions as characteristic for many other lanthanide halide complexes.

Functional alcohol complexes. The distorted pentagonal bipyramidal geometry in lanthanide(III) chloride diacetone alcohol (daa) complexes $[LnCl_3(\eta^2\text{-daa})_2]$ [Ln = Sm (**169**), Eu (**170**)] [55] show an unusual ligand arrangement, where three chloride and two alcoholic oxygen atoms of the daa molecules form the equatorial plane. The carbonyl oxygen atoms of the chelating daa molecules occupy the apical positions. This is in contrast with other reported seven-coordinated lanthanide chloride adducts with oxygen/nitrogen donor ligands such as in **147–158** [30,46,127,158–161], where two chloride occupy axial positions. Obviously the unusual ligand arrangement in $[LnCl_3(\eta^2\text{-daa})_2]$ complexes is forced by the strong intermolecular hydrogen bonds between hydrogen and chloride [Cl···O = 3.148(4)–3.166(3)] as shown in Fig. 6.

Lanthanide halide derivatives with polyalcohols of the type $(HOCH_2)_3CR$ [R = Me (Me-Glyc), $N(CH_2CH_2OH)_2$ (Dea-Glyc)] have been studied in relation with their role in the hydrolysis of phosphate diesters as well as for their luminescent properties [163–165]. The yttrium ion in $[YCl_2(\eta^3\text{-Me-Glyc})_2]Cl\cdot MeOH$ (**171**) [163] is eight-coordinate, through bonding to the oxygen donors of two tris(hydroxymethyl)ethane ligands as well as two chloride ions, and has a slightly distorted square antiprismatic geometry. Although yttrium centre is again eight-coordinate in the $[YCl_2(\eta^5\text{-Dea-Glyc})(MeOH)]Cl$ (**172**) [163], the core adopts YO_5NC1_2 coordination, defined by one nitrogen and four alcohol oxygen atoms of the ligand, a methanol oxygen atom and two chloride ions. Ligation of the bridgehead nitrogen of the ligand forces one alcoholic group to be pendant. The average Y–Cl distances are correspondingly longer in **172** than in **171**, 2.705(6) as opposed to 2.629(3) Å. In contrast to the mono complex **172** of yttrium, a *bis* complex $[La(\eta^5\text{-Dea-Glyc})_2]Cl_3$ (**173**) [164] has been isolated from a 1:1 reaction mixture of $LaCl_3$ and Dea-Glyc. The 10-coordinate environment around lanthanum centre is achieved by two η^5-ligand molecules, the three chloride ions being counter anions. Similar to **172**, one CH_2OH group attached to carbon is pendant. The Ln–O distances in **171–173**, in the range 2.321(8) to 2.622(1) Å, unambiguously establish the oxygen donors as alcoholic ROH groups rather than alkoxide RO^- groups, which characteristically fall in the 2.20–2.25 Å range.

Polyethylene glycol and crown-ether complexes. The chemistry of lanthanide halides complexes with macrocyclic polyether ligands (crown ethers) and the analogous open-chain polyethylene glycols has been well investigated, mainly in relation with their use as extractants for f-elements [11,12]. These studies show that, in general, the more flexible polyethylene glycol ligands wrap the lanthanides in a helical fashion while the crown ethers, especially the 12-crown-4 and 15-crown-5 due to their rigid cavity size, are forced to coordinate in an out-of-cavity fashion or are displaced to hydrogen bonded, outer-sphere locations if the metal ion-cavity size fit is not compatible.

The neodymium ion in the $[Nd(\eta^3\text{-deg})_3]Cl_3$ (**174**) achieves ninefold coordination with O atoms from three diethylene glycol ligands with a slightly distorted tricapped-trigonal prismatic configuration [166]. The six hydroxo-O atoms of three diethylene glycol ligands define the vertices of the trigonal prism, while the three etheroxo-O atoms cap the three rectangular faces of the trigonal prism. As expected, the Nd–O distances [2.476(4)–2.491(5) Å] for the hydroxo-O atoms are somewhat shorter than those for the etheroxo-O atoms [2.541(4)–2.583(5) Å]. The triethylene glycol ligand in the late lanthanides complexes $[LuCl_3(\eta^3\text{-treg})]$ (**175**) [167], $[LnCl_3(\eta^4\text{-treg})]\cdot MeOH$ (Ln = Tm (**176**) [168], Er (**177**), Yb (**178**) [167], Lu (**179**) [169]), $[LnCl_3(\eta^4\text{-treg})]\cdot MeCN$ (Ln = Ho (**180**), Lu (**181**) [167], Dy (**182**) [168]) and $[LnCl_3(\eta^4\text{-treg})]\cdot$18-crown-6 (a mixed treg–crown ether complex) (Ln = Y (**183**), Dy (**184**) [167,169,170]) adopts an equatorial girdle and actually mimics classic crown ether coordination. The seven-coordinate lanthanide centres in these complexes **175–184** have distorted-pentagonal-bipyramidal geometry with two chloride ions in axial positions. The solvate molecules (MeOH, MeCN, 18-crown-6), chloride ions and hydroxyl groups on triethylene glycol participate exclusively in intra- and inter-molecular hydrogen bonds to result in to polymeric chains.

The tetraethylene glycol (teg) usually forms two types of complexes; an eight-coordinate monomer with smaller europium, $[EuCl_3(\eta^5\text{-teg})]$ (**185**) [171] or a chloro-bridged dimer $[LnC1_3(\eta^5\text{-teg})]_2$ with large lanthanide (Ln = La (**186**), Pr (**187**) [171,172]), in which nine-coordinate lanthanide is in a distorted tricapped trigonal prismatic geometry. For complexes **186** and **187**, the hydroxyl groups and chloride ions participate in extensive H-bonding to give a polymeric hydrogen bonded chain of dimers. Additionally, an ionic complex $[Nd(\eta^5\text{-teg})_2]_4[NdCl_6][Cl]_9$ (**188**) [173] is also known for neodymium trichloride. The formula unit of this complex consists of four $[Nd(teg)_2]^{3+}$ cations, which are counter balanced by one $[NdCl_6]^{3-}$ and nine Cl^- anions. The 10-coordinate $[Nd(\eta^5\text{-}teg)_2]^{3+}$ cation is capped square antiprismatic. These cations pack to form large, somewhat circular channels, which contain the $[NdCI_6]^{3-}$ and Cl^- anions in such a fashion that a sheet-like structure is observed with layers of $[NdCI_6]^{3-}$ anions separating hydrophobic layers of $[Nd(teg)_2]^{3+}$ cations [173].

Both 12-crown-4 and 15-crown-5 are too small to incorporate the Ln^{3+} cations into the macrocycle cavity and thus coordinate on one side of the cation, allowing solvent molecules and chloride ions to occupy the open side of the coordination sphere. The 8-coordinate Ln^{3+} ions in the complexes such as $[LaBr_3(\eta^4\text{-}12\text{-crown-}4)(acetone)]$ (**189**) [174], $[LnCl_3(\eta^4\text{-}12\text{-crown-}4)(MeOH)]$ Ln = La (**190**) [176], Pr (**191**) [175] and $[LnCl_3(\eta^5\text{-}15\text{-crown-}5)]$ Ln = La (**192**), Ce (**193**) [177], Nd (**194**) [173], Pr (**195**) [178] sit atop the crown ether cavity and have either distorted square antiprismatic or bicapped trigonal prismatic geometry. The remarkable structure of $[Pr(\eta^5\text{-benzo-}15\text{-crown-}5)_2][I_{21}]$ (**196**) [179], obtained from the reaction of PrI_3, crown ether and I_2 in CH_2Cl_2, consists of a sandwich like cation $[Pr(\eta^5\text{-benzo-}15\text{-crown-}5)_2]^{3+}$ and a polyiodide anion $I_{21}{}^{3-}$, the latter exhibiting a complex connection pattern of iodide ions and iodine molecules with variable bond lengths thus forming a complicated network. The 18-crown-6 and dibenzo-18-crown-6, on the other hand, mimic closely the open chain polyethylene glycols and strain to fold around the lanthanide cation [180]. However, contrary to polyethylene glycol, it does not have built-in hydrogen bond donors, and also does not form directly coordinated complexes past Ln = Tb [181]. The different structural types of anhydrous 18-crown-6 complexes with the lanthanide halides are: (a) solvent-free neutral $[LaCl_3(\eta^6\text{-}18\text{-crown-}6)]$ (**197**) [181] and $[SmI_3(\eta^6\text{-dibenzo-}18\text{-crown-}6)]$ (**198**) [182]), in which nine-coordinated lanthanide centres have a tricapped trigonal prismatic geometry, (b) a solvated ionic $[GdCl_2(\eta^6\text{-}18\text{-crown-}6)(EtOH)]Cl$ (**199**) [183], and (c) an interesting $[Dy_2Cl_4(\eta^6\text{-dibenzo-}18\text{-crown-}6)_2][Dy_2Cl_8(MeCN)_2]$ (**200**) [184], where both cation and anion are chloro-bridged dimers.

3.2.2. *Complexes with nitrogen donor ligands*

3.2.2.1. Monodentate ligands. Amine complexes. The metallic scandium reacts with NH_4X (X = Br, Cl) to form *mono*- and *bis* amine complexes **201–204** [36–38] (Table S1). In $Sc(NH_3)X_3$, the scandium cation is surrounded octahedrally by five halide ions and one ammonia molecule. These $[Sc(NH_3)X_5]$ octahedra are then connected *via* two common halide edges, in accordance with the formulation $[Sc(NH_3)_{1/1}X_{1/1}X_{4/2}]$, to form a zig–zag chain [36,37]. The *bis* compounds **203** and **204** are isolated dimers in which two scandium ions have different environments and are connected *via* two bridging halides. The first scandium ion is surrounded by three NH_3 and three halide ligands, both in meridional arrangements, whereas the second scandium atom has one ammonia ligand five halide anions. These two octahedral, $[Sc(NH_3)_3X_1X_{2/2}]$ and $[Sc(NH_3)X_3X_{2/2}]$ are connected through a common halide edge [36,38]. In $(NH_4)_2[Sc(NH_3)I_5]$ (**205**), scandium ion has octahedral co-ordination with Sc–N = 2.29(2) Å and Sc–I = 2.856(5)–2.899(5) Å [39].

Pyridine and nitrile complexes. Lanthanide halides form three types of structures with pyridine: (i) a chloro-bridged dimer $[LaCl_2(\mu\text{-}Cl)(py)]_2$ (**206**), in which lanthanum centres are eight-coordinated [59], (ii) monomeric $[LnCl_3(py)_4]$ (Ln = Y (**207**), Eu (**208**) [60]) and $[LnCl_3(py)_4]\cdot(1/2)py$ (Ln = La (**209**), Er (**210**) [60a], Yb (**211**) [33]), where seven-coordinate lanthanide atoms adopt a pentagonal-bipyramidal geometry with axial positions being occupied by two chloride ions, and (iii) ionic complexes $[LnI_2(py)_5]I$ (Ln = Yb (**212**) [96] and Lu (**213**) [43]. The lutetium metal in **213** is seven-coordinated, although still maintaining an ionic structure. In contrast, even if heptacoordination is feasible for lutetium complexes, the isopropanol adduct $[LuI_2(Pr^iOH)_4][I]$ (**82**) [43] prefers to only bind to two of the three iodide ligands and thus remaining six-coordinated. This difference in binding may be traced to the relative donor strengths of pyridine versus isopropanol. The tendency of lanthanide halides to undergo auto-ionization is further reflected in their *N*-methylimidazole (N-MeIm) complexes **214–217**, where $[YX_2(N\text{-MeIm})_5]^+$ and $[Sm(N\text{-MeIm})_8]^{3+}$ cations are counter-balanced by either $[YX_4(N\text{-MeIm})_2]^-$ or X^- anions (X = Cl, Br, I) [118,185] (Table S1).Using acetonitrile as ligand, a remarkable ionic structure $[YbCl_2(MeCN)_5]_2[YbCl_3(MeCN)(\mu\text{-}Cl)_2YbCl_3(MeCN)]$ (**218**) has been observed for ytterbium trichloride, where two pentagonal-bipyramidal $[YbCl_2(MeCN)_5]^+$ cations with apical chloride ions are charged balanced by an octahedral dinuclear $[YbCl_3(MeCN)(\mu\text{-}Cl)_2YbCl_3(MeCN)]^{2-}$ anion with MeCN ligands in transoid positions [30].

3.2.2.2. Potential bi- and polydentate ligands. Pyridine-based and related ligands. With bi-pyridine ligand, a eight-coordinate binuclear complex $[(\eta^2\text{-bipy})_2Cl_2La(\mu\text{-}Cl)_2LaCl_2(\eta^2\text{-bipy})_2]\cdot EtOH$ (**224**) for larger lanthanum atom and a totally unsolvated array for smaller seven-coordinate ytterbium $[(\eta^2\text{-bipy})_2YbCl_3]$ (**225**) are isolated [190]. The eight-coordinate cerium and uranium atoms in the molecule $[MI_3(\eta^2\text{-bipy})_2(py)]\cdot x$ py [M = Ce ($x = 5$) (**226**), U ($x = 2$) (**227**)] are surrounded by five nitrogen atoms of one pyridine and two bidentate bipyridine ligands, and by three iodide ligands [191]. Potentially tridentate terpyridine-functionalized ligands (terpy and R-btp) have been shown to have higher selectivity for An(III) over Ln(III) than bipy in numerous competition and liquid–liquid extraction studies. Addition of two equivalents of terpy to $[MI_3(py)_4]$ (M = Ce, Nd, U) in anhydrous pyridine gave the complexes $[MI_2(\eta^3\text{-terpy})_2]I\cdot 2py$ [M = Ce (**228**), Nd (**229**)] and $[UI_2(\eta^3\text{-terpy})_2(py)]I\cdot 2py$ (**230**) which are unique examples of bis-terpy compounds of the early lanthanides and uranium [192] (Fig. 7). In the crystal structure of **230**, an indication of the presence of a π back-bonding interaction between the trivalent 5f ion and the aromatic nitrogen ligand is given by the U–N(central pyridine) distances [2.602(1)–2.618(9) Å], which are shorter than the U–N(distal pyridine) distances [2.624(9)–2.657(1) Å], while the reverse situation is observed in the early lanthanide terpy complexes.

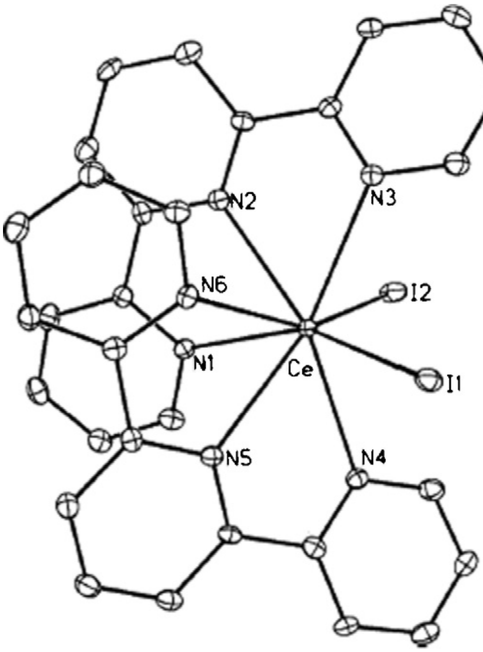


Fig. 7. Structure of [$CeI_2(\eta^3$-terpy$)_2$]I (**228**). Reproduced from Ref. [192] by permission of the Wiley–VCH.

Further evidences of this better affinity and selectivity of tridentate terpy and R-btp ligands for UI_3 over LnI_3 have been provided by the crystal structures of *tris*-derivatives [$Ln(\eta^3$-terpy$)_3$]$I_3 \cdot x$MeCN ($x = 2$, Ln = La (**231**), Ce (**232**), Nd (**233**); $x = 3$, Ln = Ce (**234**) [193]), [$U(\eta^3$-terpy$)_3$]I_3·2MeCN (**235**) [193], [$Ce(\eta^3$-Mebtp$)_3$]I_3·9py (**236**) [194], [$Ce(\eta^3$-Pr^nbtp$)_3$]I_3·3py (**237**) [193,194] and [$U(\eta^3$-Pr^ntp$)_3$]I_3·4py (**238**) [193,194], where the U–N distance is shorter than the Ln–N distance by 0.06–0.09 Å, suggesting that U–N π back donation plays an important role in the overall bonding (Fig. 8) (Table S1). In all cases, this structural difference was more pronounced for the R–btp complexes than in those derived from terpy [193,194]. This order of selectivities, bipy < terpy < btp, corresponds to the order of the differences between the U–N and Ce–N bond lengths in the crystal structures of analogous U(III) and Ce(III) complexes. The versatility of pybox ligands has been demonstrated in numerous catalytic asymmetric syntheses and the enantioselective catalysis with pybox complexes has been reviewed recently [195]. Lanthanide(III) chloride complexes with Pr^i-pybox ligand are ion-pairs of the type, [$LnCl_2(\eta^3$-Pr^i-pybox$)_2$][$LnCl_4(\eta^3$-Pr^i-pybox)] [Ln = Eu (**239**), Yb (**240**)], with a distorted dodecahedral and a pentagonal bipyramidal geometry around eight- and seven-coordinate lanthanide atoms, respectively [196].

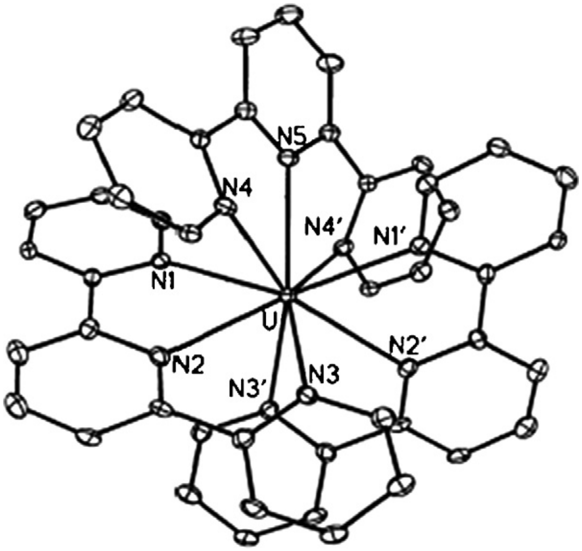


Fig. 8. Structure of *mer*-[$U(\eta^3$-terpy$)_3$]I_3 (**235**). Reproduced from Ref. [193] by permission of the Royal Chemical Society.

Both *mono*- and *bis*-complexes of Ln(III) and U(III) halides with potentially tetradentate ligand tpa are known [197–200]. The seven-coordinated lanthanide atoms in [$Ln(\eta^4$-tpa$)Cl_3$] (Ln = Eu (**241**), Tb (**242**), Lu (**243**) [197]) and [$Ce(\eta^4$-tpa$)I_3$] (**244**) [198] have distorted monocapped octahedral geometries. In [$La(\eta^4$-tpa$)I_3$(py)] (**245**) and [$U(\eta^4$-tpa$)I_3$(py)] (**246**), on the other hand, the eight-coordinate metal center is in a highly distorted dodecahedral environment [199]. The *bis*-derivatives [$Ln(\eta^4$-tpa$)_2$]I_3 (Ln = La (**247**), Ce (**248**), Nd (**249**), Lu (**250**) [198]) and [$U(\eta^4$-tpa$)_2$]I_3·3MeCN (**251**) [200] have eight-coordinated metals in a distorted cube geometry with the two tpa ligands adopting a right-handed helical arrangement, thus creating a chiral species. A comparison of the mono-tpa complexes **245** and **246** reveals that one pyridyl group had a shorter than expected U–N distance, suggesting a covalent interaction between tpa and U(III). Otherwise, only minimal differences in the M–N length between La and U for the ligand (tpa) have been observed [199]. The softer character of the tpza ligand is believed to lead to stronger, and possibly more covalent, interactions with the actinides. In contrast to ligand tpa, the other potentially tetracoordinate ligand tpza forms only 1:1 complexes with Ln(III) and U(III), i.e. [$La(\eta^4$-tpza$)I_3$(MeCN)]·MeCN (**253**), [$U(\eta^4$-tpza$)I_3$(MeCN)]·MeCN (**254**), [$La(\eta^4$-tpza$)I_3$(thf)]·thf (**278**), [$U(\eta^4$-tpza$)I_3$(thf)]·thf (**279**), suggesting that it binds these cations less strongly than tpa, most likely due to its lower donor ability [201]. X-ray diffraction studies on these tpza derivatives reveals that whereas the Ln–N(tpza) distance remains unaffected in acetonitrile adducts **253** and **254**, the largest difference occurs in the M–N(MeCN) bond; the U–N(MeCN) distance was 2.610(1) Å while the La–N(MeCN) distance was 2.662(4) Å. In addition, the length of the N–C (acetonitrile) bond increased in the uranium complex (it normally shortens upon coordination). In the case of thf complexes [$La(\eta^4$-tpza$)I_3$(thf)]·thf (**278**) and [$U(\eta^4$-tpza$)I_3$(thf)]·thf (**279**), shortened Ln–N(tpza) bonds were generally found for the uranium complex relative to the corresponding lanthanum species (the average decrease is 0.046 Å), indicating that the uranium cation is held more tightly than the lanthanum cation. It was also suggested that acetonitrile, which can act as a π-acceptor ligand, competes with the tpza for electron back donation from the uranium(III) center. On the other hand, thf is a σ-donor and no such competition occurs, allowing back donation from the uranium cation to the ligand, which, in turn, leads to shorter U–N(tpza) distances. DFT calculations produced similar results, namely a decrease in the M–N(tpza) distance upon passing from lanthanum to uranium, as well as an increase in the C–N distance for the uranium–acetonitrile complex [201].

Two different types of crystals were obtained for the lanthanide(III) halide complexes of potentially hexadentate ligand tpztn by slightly changing the crystallization conditions. The structures of $[\mathrm{La}(\eta^6\text{-tpztn})\mathrm{I_2}]\mathrm{I}$ (**255**), isolated from an acetonitrile/isopropyl ether solution, as well as $[\mathrm{Ln}(\eta^6\text{-tpztn})\mathrm{I_2}]\mathrm{I}\cdot 1.17\mathrm{MeCN}$ [Ln = La (**256**), Ce (**257**), Nd (**258**)] and $[\mathrm{U}(\eta^6\text{-tpztn})\mathrm{I_2}]\mathrm{I}\cdot 1.17\mathrm{MeCN}$ (**259**) isolated from a concentrated acetonitrile solution, reveal two different geometric isomers of the cation $[\mathrm{Ln}(\eta^6\text{-tpztn})\mathrm{I_2}]^+$. In both types of structures, the metal is eight-coordinated by the six nitrogen atoms of η^6-tpztn ligand and two iodide ions [202]. However, the ligand arms wrap around the metal center in two different ways to give different geometries, i.e. a distorted dodecahedron in **255** and a distorted square antiprism. The chiral complexes **256–259** crystallize as a racemic mixture of Λ,Λ and Δ,Δ enantiomers. The Lu complex $[\mathrm{Lu}(\eta^6\text{-tpztn})(\mathrm{MeCN})_2]\mathrm{I_3}\cdot\mathrm{MeCN}$ (**260**) shows a different coordination environment with respect to the lighter lanthanides. The lutetium ion is eight-coordinated by the hexadentate ligand tpztn and by two nitrogen atoms from two acetonitrile molecules with a slightly distorted square antiprismatic geometry. The absence of coordinated iodide ions for Lu can be explained by an increased steric congestion around this smaller and more electropositive ion which prevents coordination of the large iodide ions. The higher tendency of lutetium iodide complexes to undergo auto-ionization has previously been reported [43]. Other lanthanide(III)/uranium(III) iodide complexes with tpzcn ligand namely $[\mathrm{Ln}(\eta^6\text{-tpzcn})\mathrm{I_2}]\mathrm{I}\cdot 0.5\mathrm{MeCN}$ [Ln = La(**261**), Ce (**262**), Nd (**263**)] and $[\mathrm{U}(\eta^6\text{-tpzcn})\mathrm{I_2}]\mathrm{I}\cdot 0.5\mathrm{MeCN}$ (**264**) are isostructural with those of **256–259** [202]. The uranium(III) iodide complex $[\mathrm{U}(\eta^7\text{-tbpa})\mathrm{I_2}]\mathrm{I}\cdot\mathrm{py}$ (**265**) with a heptadentate tbpa ligand consists of cation–anion pairs and a molecule of pyridine connected by H-bonding to three different cations and one anion [203]. The uranium metal has a distorted capped square antiprismatic geometry (Fig. 9).

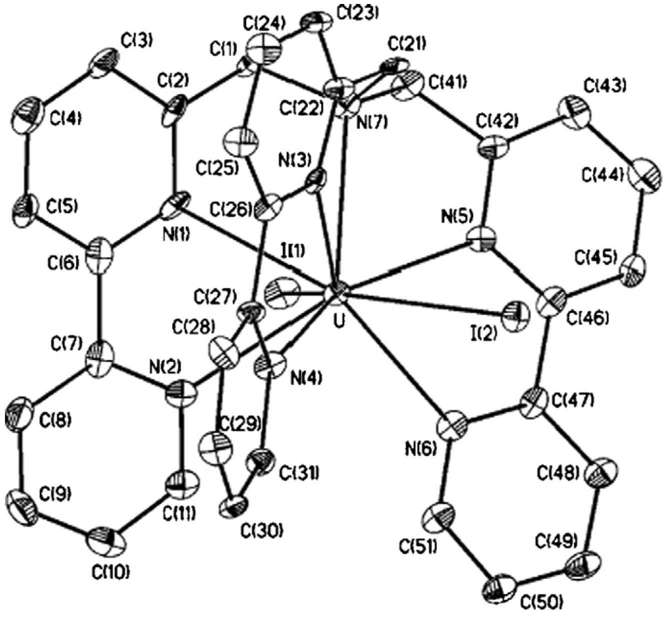
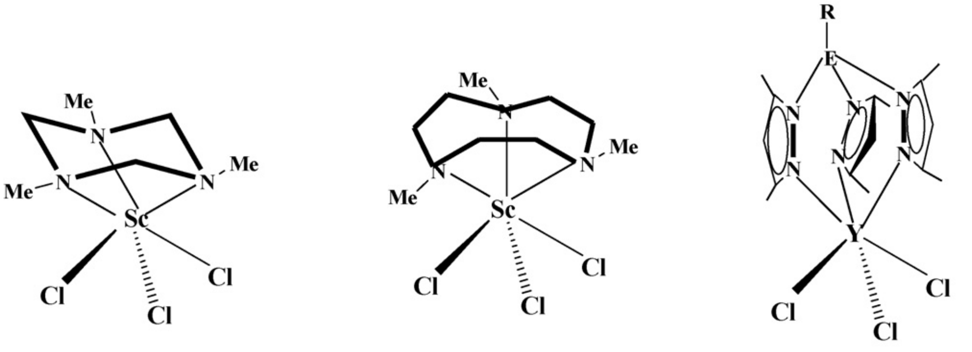


Fig. 9. Structure of $[\mathrm{UI_2}(\eta^7\text{-tbpa})]\mathrm{I}\cdot\mathrm{py}$ (**265**). Reproduced from Ref. [203] by permission of the Royal Chemical Society.

Miscellaneous ligands. The six electron donor bearing three amines in a cyclic array provided by the triazacycloalkane ligands such as $\mathrm{Me_3[6]aneN_3}$ and $\mathrm{Me_3[9]aneN_3}$ have found notable applications as a facially coordinating neutral ancillary ligands. In 1997 Bercaw and coworkers described the use of this ligand system in scandium chemistry [204]. Both $[\mathrm{Sc}(\eta^3\text{-Me_3[6]aneN_3})\mathrm{Cl_3}]$ (**266**) [205] and $[\mathrm{Sc}(\eta^3\text{-Me_3[9]aneN_3})\mathrm{Cl_3}]$ (**267**) [204] are half-sandwich compounds with comparable Sc–N bond distances but significantly different Sc–Cl bond lengths (av. 2.377 in **266** ver. 2.404 in **267**) (Fig. 10). Work of a similar nature has been carried out recently by Mountford et al. using the neutral *fac*-coordinating *tris*-(pyrazolyl)methane and -methylsilane ligands [205]. The structures of $[\mathrm{Y}\{\mathrm{HC}(3,5\text{-Me_2pz})_3\}\mathrm{Cl_3}]\cdot 2\mathrm{MeCN}$ (**268**) [206] and $[\mathrm{Y}\{\eta^3\text{-MeSi}(3,5\text{-Me_2pz})_3\}\mathrm{Cl_3}]\cdot\mathrm{CH_2Cl_2}$ (**269**) [205] are similar with comparable Y–Cl and Y–N bond distances. The six-coordinate yttrium centers in **268** and **269** can best be regarded as trigonal antiprismatic with one tighter triangle defined by the nitrogen atoms and with a more open one defined by the chloride groups (Fig. 10). By contrast, the larger samarium accommodates an additional thf ligand to give a

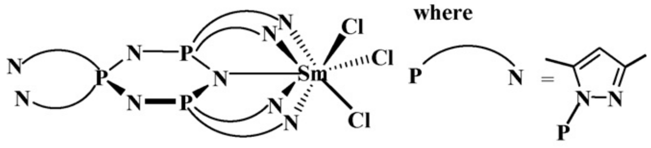


(**266**)

(**267**)

(**268**): E = C, R = H
(**269**): E = Si, R = Me

Fig. 10. Structures of $[\mathrm{Sc}(\eta^3\text{-Me_3[6]aneN_3})\mathrm{Cl_3}]$ (**266**), $[\mathrm{Sc}(\eta^3\text{-Me_3[9]aneN_3})\mathrm{Cl_3}]$ (**267**), $[\mathrm{Y}\{\mathrm{HC}(3,5\text{-Me_2pz})_3\}\mathrm{Cl_3}]\cdot 2\mathrm{MeCN}$ (**268**) and $[\mathrm{Y}\{\eta^3\text{-MeSi}(\mathrm{Me_2pz})_3\}\mathrm{Cl_3}]\cdot\mathrm{CH_2Cl_2}$ (**269**).



(270)

Fig. 11. Structure of $[Sm\{\eta^5\text{-}\textit{hexakis}\text{-}(Me_2pz)cytp\}Cl_3]$ (**270**).

seven-coordinate $[Sm\{HC(3,5\text{-}Me_2pz)_3\}Cl_3(thf)]\cdot thf$ (**276**), the geometry of which may be described in two alternative ways: (a) as a trigonal antiprism defined by the $HC(3,5\text{-}Me_2pz)_3$ and Cl groups, with the thf capping the triangular face defined by the Cl ligands; (b) as a tricapped trigonal pyramid, with the three nitrogen atoms of the $HC(3,5\text{-}Me_2pz)_3$ ligand defining the base and the thf oxygen at the apex position [206]. In the latter view, the chloride ions cap the three faces of the pyramid. The average Sm–Cl distance, 2.621 Å is broadly similar to that observed in other seven-coordinate samarium chloride complexes such as $[SmCl_3(thf)_4]$ (**46**) (2.657 Å) [127].

Single crystal X-ray structure of $[Sm\{\eta^5\text{-}(3,5\text{-}Me_2pz)_3Cytp\}Cl_3]$ (**270**) [207] reveals unprecedented pentadentate coordination behavior of the *hexakis*-(3,5-dimethylpyrazolyl)cyclotriphosphazene ligand. One cyclophosphazene ring nitrogen atom N(1) and four pyridine nitrogen atoms N(12), N(22), N(32) and N(42) from two sets of geminal pyrazole substituents on P(1) and P(2) constitute the η^5-N binding core to coordinate $SmCl_3$, forming an eight-coordinate complex, with a distorted hendecahedral geometry (Fig. 11). This kind of complexation causes P_3N_3 ring puckering. The samarium atom interacts more strongly with *hexakis*-(Me_2pz)Cytp ligand *via* the phosphazene ring nitrogen atom N(1) than *via* the pyridine nitrogen atoms: the average $Sm–N_{ring}$ bond distance of 2.499 Å is shorter than that of $Sm–N_{pyz}$ distance of 2.832 Å.

3.2.3. Complexes with mixed oxygen and nitrogen donor ligands

Both $[LaCl_3(de\text{-}hipp)_3]$ (**280**) [209] and $[PrCl_3(dip\text{-}hipp)_3]$ (**281**) [210] have similar nine-coordinate geometry around the Ln^{3+} ion, which may be envisaged as tricapped-trigonal prismatic with the three capping positions occupied by imine nitrogen atoms, with relatively long Ln–N bonds [av. 2.851(9) Å (**280**) and 2.798(7) Å (**281**)]; the oxygen atoms form one end of the trigonal prism [av. Ln–O 2.512(9) Å (**280**) and 2.461(9) Å(**281**)] and the three chloride ions form the other end [av. La–Cl 2.860(5) Å (**280**) and 2.784(4) Å (**281**)]. Both compounds show hydrogen-bonding between the oxime hydrogen atom and the chloride ligand [mean $O(H)\cdots Cl = 2.983$ Å (**280**) and 2.916 Å (**281**)], effectively forming pseudo five-membered chelate rings. With a heptadentate O_3N_4 ligand, tpaam, a nine-coordinate complex $[LaI_2(\eta^7\text{-}tpaam)]I\cdot 0.25\,py$ (**282**) for larger lanthanum metal and a eight-coordinate complex $[LuI(\eta^7\text{-}tpaam)]I_2\cdot 0.25\,MeCN\cdot 0.5py$ (**283**) for smaller lutetium atom have been isolated [211]. In the X-ray structure of $[LaCl_2(\eta^7\text{-}cryptate\{2.2.1\}]Cl\cdot MeOH$ (**284**), the cryptand ligand and two chloride anions form an inner-sphere complex, and a molecule of methanol fills the space. The encryptated metal ion is nine-coordinated, and all the heteroatoms of the cryptate (2.2.1) ligand coordinate the metal center to form a bowl-shaped structure. Two coordinating chloride ions are located on the open face with a *cis* geometry [212]. Important X-ray crystallographic data including some selected bond lengths of the complexes described in the Section 3.2 and few other Ln(III) halide complexes with miscellaneous ligands [151,153,156,157,162,187–189,208] are given in Table S1.

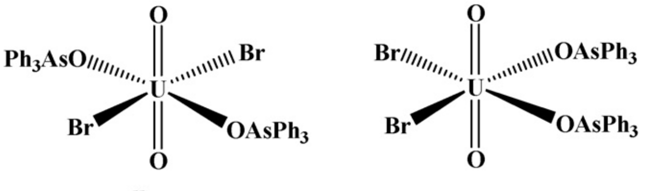
3.3. Actinide(IV), -(V) and -(VI) halide complexes

Actinide(IV), -(V) and -(VI) as well as mixed-valent -(III)/(IV) halide complexes with oxygen and nitrogen-donor ligands are either molecular compounds or ion-pairs, where coordination geometry around the metal is dictated by the basicity and steric demand of the Lewis base (Table S2).

3.3.1. Complexes with oxygen donor ligands

3.3.1.1. Monodentate ligands. Tetrahydrofuran complexes. The tetravalent uranium chloride forms two types of thf adducts, $[UCl_4(thf)_3]$ (**285**) [213] and $[UCl_3(\mu\text{-}Cl)(thf)_2]_2$ (**286**) [214], the uranium ion having distorted pentagonal bipyramidal geometry in both cases. In contrast, eight-coordinate the thorium centre in $[ThBr_4(thf)_4]$ (**287**) [71] has a dodecahedral geometry. Similar to U(IV) chloride, uranyl halides too exist either in dimeric $[UO_2Cl_2(thf)_2]_2$ (**288**) [81] or monomeric $[UO_2X_2(thf)_3]$ (X = Cl (**289**) [82], Br (**290**) [83], I (**291**) [79]) forms. Additionally, an ion-pairs $[UO_2Cl(thf)_4][UCl_5(thf)]$ (**292**) [215] containing mixed-valent U(VI)/U(IV) species is also known. The two imido analogs of the uranyl halide complexes **289–291**, i.e. $[UI_2(=NBu^t)_2(thf)_2]$ (**293**) [88] and $[UI_2(=NPh)_2(thf)_3]$ (**294**) [88] have an octahedral and a pentagonal bipyramidal geometry, respectively. The two imido ligands in **293** and **294** exhibit a *trans* geometry (N1–U–N2 = 175.4–177.4°), which is rare even in transition metal chemistry. The U–N bond distances in **293** and **294** (av. 1.853 Å) are significantly shorter than the average U–N interactions reported for $[PPh_4][UOCl_4(NSPh_2)]$ (1.916 Å) and $[Cp^*_2U(NPh)_2]$ (1.952 Å) [88].

Trialkylphosphineoxide and related complexes. Sterically demanding trialkyl-phosphine and -arsine oxide ligands usually form molecular compounds of the types $AnX_4(L)_2$ [219,220,223–227] and $[AnO_2X_2L_2]$ [78,84–86,222] (An = U, Th, Np; X = Cl, Br, I; L = tppo, typrpo, teao, tpao, ebdpao) in which the actinide metal has either regular or slightly distorted octahedral environment (complexes **298**, **299**, **301–304**, **306–312** and **314** in Table S2). Formations of ionic complexes of the types $[UCl(tmpo)_6]Cl_3$ (**297**) and $[UO_2(L)_4](X_3)_2$ [L = tppo (X = I) (**305**), tpao (X = Br) (**313**) have also been reported using less sterically demanding trimethylphophine oxide ligand [218] or excess of molecular bromine or iodine, which results into formation of X_3^- counter ions [80]. The only known penta-valent uranium halide complex with O-donor ligand $[UCl_5(tppo)]$ (**300**) has an octahedral geometry [221]. The above *bis*-complexes usually present the expected *all-trans* octahedral geometry [84–86,220,222–227]. However, depending



all-trans *cis-trans*

Fig. 12. Structures of (a) *all-trans* and (b) *cis–trans* isomers of $[UO_2Br_2(tpao)_2]$.

upon conditions of crystallization, a *cis*-$[UCl_4(tppo)_2]$ (**298**) [219] as well as both *all-trans*- and *cis–trans* isomers for $[UO_2Cl_2(tppo)_2]$ [85] and $[UO_2Br_2(tpao)_2]$ [78] (Fig. 12) have also been isolated. For $[UO_2Br_2(tpao)_2]$, the *all-trans* isomer forms under normal conditions but complete isomerization of *all-trans* to *trans–cis* takes place when a suspension of the former in methanol is stirred at rt for several hours [78].

Hexamethylphosphoramide and related complexes. Similar to trialkyl-phosphine and -arsine oxide complexes **298**, **299**, **301–304**, **306–312** and **314**, actinide halide complexes with hmpa and related ligands are mostly six-coordinated, rich in *trans*-geometry, molecular compounds of the types $AnX_4(L)_2$ [228,229,231,234–236,238] and $[AnO_2X_2L_2]$ [76,84] (An = U, Th; X = Cl, Br, I; L = hmpa, ptmpa, omppa, dmdpu, tmu, dmpva) (complexes **315–319**, **321**, **324–328**, **330**, **332** and **333** in Table S2). Additionally, a pentagonal bipyramidal geometry is found for complexes $AnCl_4(L)_3$ [An = Th; L = depa (**322**), dmdpu (**329**)] [232,237]. In certain cases, formation of ionic complexes $[UO_2(hmpa)_4](I_3)_2$ (**320**) [230] and $[UCl_3(depa)_4][UCl_5(depa)]$ (**331**) [239] were also observed.

Dialkyl formamide, -sulfoxide and other miscellaneous complexes. The eight-coordinate actinide atoms in molecular $[AnCl_4(PriOH)_4]$ [An = U (**295**), Th (**296**)] [216] have a distorted square antiprismatic geometry. Except *trans*-$[UCl_4(dibso)_2]$ (**334**) [223] and $[UO_2Cl_2($*tert*-butylformamide$)_3]$ (**338**) [243], all other dialkyl formamide and -sulfoxide complexes of actinides namely $[UCl_2(dmso)_6][UCl_6]$ (**335**), $[UCl(dmso)_7]Cl_3$ (**336**), $[UCl_3(dmf)_5]_2[UCl_6]$ (**337**) and $[U(dmso)_9]I_4$ (**339**) are ionic, where $[U(L)_xX_y]^{n+}$ (L = dmf, dmso, X = Cl, I) cations are charge-balanced by X^- or $[UCl_6]^{2-}$ anions [75,240–242].

3.3.1.2. Potential bi- and polydentate ligands. The eight-coordinate thorium atoms in $[ThCl_4(\eta^2\text{-omppa})_2]$ (**323**) [233] and $[ThBr_4(\eta^2\text{-dme})_2]$ (**340**) [244] have square antiprismatic and dodecahedral geometries, respectively. Th-X [2.725(8)–2.871(1) A] (X = Cl, Br) and Th-O [2.412(6)–2.620(8) A] distances are all unexceptional and can be compared to those observed in other eight-coordinate Th(IV) halide complexes [71,216]. In the nine-coordinate cations of $[UCl_3(\eta^6\text{-dicyclohexyl-18-crown-6})]_2[UCl_6]$ (**341**) [245], uranium atoms are bonded to all six oxygen donors of crown ether as well as three chloride ions. The counteranion is a well-known $UCl_6{}^{2-}$. The other hexadentate ligand, i.e. pentaethylene glycol wraps the thorium ion in $[ThCl_3(\eta^6\text{-peg})]Cl\cdot MeCN$ (**342**) [246], resulting in a tricapped trigonal prismatic geometry for the metal center. As observed previously, the average Th–O(alcoholic) bond distance, 2.49(1) Å, is somewhat shorter than the Th–O(etheric) bond lengths (2.57(4) Å). The ionized chloride ions form intermoleculr H-bonding with alcoholic oxygen atoms, resulting into zig–zag polymeric chain along the *c*-axis [246].

3.3.2. Complexes with nitrogen donor ligands

3.3.2.1. Monodentate ligands. Pyridine and amine complexes. The actinide centres of $[UI_4(py)_3]$ (**343**) [75], $[UO_2I_2(py)_3]$ (**344**) [79] and $[ThCl_4(tma)_3]$ (**345**) [247] have a classical pentagonal bipyramidal geometry, with either the linear UO_2 (**344**) or AnX_2 (**343**,**345**) fragments perpendicular to the equatorial plane defined by the three nitrogen atoms of the pyridine/tma ligands and two non-adjacent halide groups. The average U–I distance is shorter in **343** (3.00 Å) than in **344** (3.111 Å), though a reverse pattern is observed for the U–N bond lengths (2.607 Å in **343** ver. 2.543 Å in **344**). The structures of *trans*-$UO_2Cl_2(NHPPh_3)_2$ (**346**) and *trans*-$UO_2Cl_2(NHPCy_3)_2$ (**347**) are similar, with the uranium occupying the center of a distorted octahedron and showing comparable U–O, U–Cl and U–N bond distances [86,87]. Surprisingly, *cis*-$UO_2Cl_2(NHPCy_3)_2$ (**348**) [86], which has greater steric interactions, exhibits unusual shortening of all the equatorial ligand–uranium bond lengths compared to *trans*- complex **347**, e.g., the U–Cl and U–N bond distances in *cis* isomer **348** are 2.350(2) and 2.686(7) Å, respectively, compared to 2.704(2) and 2.392(5) Å for *trans* isomer **347**.

Nitrile complexes. Contrary to the neutral $UX_4(MeCN)_4$ [X = Cl (**349**), Br (**350**)] [248,249], the formation of an ionic species $[UI_2(MeCN)_7][UI_6]$ (**351**) [75] is in accordance with earlier observations on the “soft” nature of the iodide atom and the ease with which the iodide ligand can be removed. An eight-coordinate U(IV) atom in $UI_4(CNPh)_4$ (**352**) [72] shows a “puckered” square antiprismatic geometry, which is significantly different from the dodecahedral geometry found in **349** [248]. Both mixed-valent U(III)/U(IV) compounds $[U(NCMe)_9][UI_6][I]$ (**353**) and $[UI(NCPh)_8][UI_6]$ (**354**) are ion-pairs, where nine-coordinate U(III) atoms in cations have an ideal tricapped trigonal prismatic and a highly distorted monocapped square antiprismatic geometry, respectively [72].

3.3.2.2. Potential bi- and polydentate ligands. In contrast to dodecahedral $[ThBr_4(\eta^2\text{-dme})_2]$ (**340**) [244], the geometry of eight-coordinate $[AnCl_4(\eta^2\text{-tmeda})_2]$ (An = U (**355**) [250], Th (**356**) [251] is a slightly distorted square antiprism. The U–N bond distances in **355** [2.769(1)–2.809(9)] are considerably longer than the ones found in **349** [2.567(6)–2.599(6)] [248]. The $[UF_5(\eta^2\text{-bipy})]$ (**357**) [252] is the only known penta-valent uranium halide complex with N-donor ligand. Two forms of this compound, a monoclinic and an orthorhombic, was established by single-crystal X-ray studies. The coordination of the uranium atom in both forms is a distorted monocapped trigonal prism with one fluorine atom occupying the capping site. The main difference is found in the packing of the molecular unit $UF_5.bipy$; in monoclinic form all the molecular units are in the same orientation and form successive layers of UF_5 and bipy, whereas, in orthorhombic form, the molecules pack in head-to-tail fashion.

Using a tridentate mixed O- and N-donor tipc ligand, *cis*-dihalide uranyl derivatives $[UO_2X_2(\eta^3\text{-tipc})]$ [X = Cl (**358**), Br (**359**)] have been isolated recently [77]. Other *cis* compounds $[UO_2Cl_2(tppo)_2]$ (**302**), $[UO_2Br_2(tpao)_2]$ (**312**) and $[UO_2Cl_2(NHPCy_3)_2]$ (**348**) have been reported to form along with *trans* isomer, depending upon the condition of crystallization [78,85,86]. Given the synthetic importance of stereochemical control in lanthanide halide systems, preparation of the above compounds **358** and **359** serves as a rational methodology to anhydrous uranyl(VI) *cis*-dihalide complexes that can serve as suitable starting materials with reagents in non-protic solvents.

3.4. Heterometallic lanthanide and actinide halide complexes

The main group metal chlorides such as $AlCl_3$, $SnCl_4$, $SbCl_5$ are clean and convenient halide abstracting agents for lanthanide(III) chlorides, which depending on the stoichiometry used and the choice of solvent (S), can provide a variety of solvated heterometallic lanthanide halide complexes following single and/or multiple removal of chloride ion(s). The smaller scandium is six-coordinate in $[ScCl_2(thf)_4][SnCl_5(thf)]$ (**360**) [90] and features a *trans*-$ScCl_2$ axial unit with four thf molecules in an equatorial girdle to give an octahedral metal geometry. On the other hand, other lanthanide metals form seven-coordinate *trans*-$[LnCl_2(thf)_5][SnCl_5(thf)]$ (Ln = Ce (**361**), Gd (**362**), Yb (**363**) [91], Pr (**364**) [92]) with a pentagonal bipyramidal metal geometry. The equatorial LnO_5 segments are coplanar in **361–364**, where the quintets of thf molecules adopt the familiar 'propellor-like' arrangement. There is a discernible shortening in both the Ln–Cl and the Ln–O bond distances from **361** to **363**, consistent with the recognized atomic size contraction across the series. The $[SnCl_5(thf)]^-$ anion, which is known to show some subtle structural variation within the confines of the octahedral geometry, is notably similar in **361–364**. Transition metal halides, essentially the ones which are Lewis acid in nature, have also been employed for halide abstraction and complexes of the type $[YbCl_2(thf)_5][WOCl_4(thf)]$ (**365**) [253], $[LaCl(tppo)_5][FeCl_4]_2$ (**366**) [94] and $[GdCl_2(tppo)_4][CuCl_3]$ (**367**) [95] isolated. In comparison to a pb geometry found with thf ligand in **361–365**, the bulkier triphenyl phosphine oxide ligand forces lanthanide atoms to adopt a distorted octahedral environment in **366** and **367** [94,95].

In complexes $[Ln(MeCN)_9][AsF_6]_3{\cdot}x MeCN$ [Ln = La ($x = 1$) (**368**), Sm ($x = 3$) (**369**)] [89], $[Ln(MeCN)_9][AlCl_4]_3{\cdot}MeCN$ [Ln = Pr (**370**), Sm (**371**)] [89,93], and $[Pr(MeCN)_9][SnCl_5(thf)]_{2.5}[SnCl_5(MeCN)]_{0.5}$ (**374**) [92], the tricapped trigonal prismatic geometry of homoleptic nine-coordinate lanthanide cation is essentially unaffected by the nature of anions. The Ln–N distances show little variation in **368–371** and **374**, with no significant difference between bonds to the capping and prismatic donor atoms (Table S3). This is in marked contrast to the corresponding homoleptic aqua cations $[Ln(H_2O)_9]^{3+}$, which are also tricapped trigonal prismatic but with discernible differences between $Ln\text{–}O_{prism}$ and $Ln\text{–}O_{capping}$ [217]. In **374**, two of the three counteranions are regular $[SnCl_5(thf)]^-$ moieties, as observed for **360–364**, whereas the third counteranion shows half-occupancy at the solvent position between thf and MeCN molecules. The tin centre in this third anion retains an octahedral geometry, with Sn–O(thf) [2.308(1) Å] and Sn–N(MeCN) [2.276(1) Å]. As a result of lanthanide contraction, the complex $[Yb(MeCN)_8][AlCl_4]_3$ (**372**) [89] has dodecahedral eight-coordination for ytterbium. In contrast to the tricapped trigonal prismatic geometry found in **368–371**, the praseodymium centre of $[Pr(MeCN)_9][SnCl_5(MeCN)]_3$ (**373**) adopts a rare mono-capped square prismatic (cubic) geometry, which is slightly distorted [92]. Also, there is a slight elongation for the $Pr\text{–}N_{capping}$ bonds [2.645(2) Å] in comparison to the $Pr\text{–}N_{prism}$ bonds [2.502(9)–2.583(9) Å]. The octahedral $[SnCl_5(MeCN)]^-$ counter anion, however, is quite similar to that of $[SnCl_5(thf)]^-$ anion observed in **360–364**.

Use of iodide in place of chloride anion is relatively a new phenomenon in heterometallic lanthanide halide complexes with donor ligands [96–100]. The soft and bigger iodide anion, which often undergoes auto-ionization in lanthanide iodides, not only helps in the formation of heterobimetallic lanthanide iodide derivatives but also results in interesting structural features due to its versatile coordination modes [98–100]. Unlike most of the heterometallic halide derivatives, which are ion-pairs (Table S3), the structure of $[(thf)_5NdI(\mu\text{-}I)HgI_3]$ (**375**) [96] has neodymium and mercury centres bridged by an iodide. As observed for **360–365**, neodymium ion has a pb geometry with two axial I^- and five equatorial thf ligands, whereas environment around Hg centre is that of a distorted tetrahedral. As expected, the $Hg\text{–}I_{bridging}$ distance [3.245(5) Å] is much longer than the $Hg\text{–}I_{terminal}$ bonds [av. 2.720 Å]. However, this difference is not apparent for neodymium moiety, where $Nd\text{–}I_{bridging}$ distance [3.108(6) Å] is almost similar to the $Nd\text{–}I_{terminal}$ bond [3.054(6) Å]. In contrast, the more acidic ZnI_2 abstracts an iodide from LnI_3 completely and gives an ion-pairs of the type $[(thf)_5NdI_2][(thf)ZnI_3]$ (**376**), where the structures of both cation and anion find considerable precedence in the literature [96]. The eight-coordinate yttrium atom in the cation of $[Y(dmso)_8][Cu_2I_5]$ (**378**) [98] has a regular square antiprism geometry. The charge balance for this cation is provided by a dinuclear $[Cu_2(\mu\text{-}I)I_4]^{3-}$ cluster. This perfectly planar cluster has four iodide ligands terminally bonded to two trigonal planar Cu(I) centres, which are bridged by a μ-I. As expected, the Cu–μ-I (av. 2.60 Å) bond distances are longer than the terminal Cu–I ones (av. 2.52 Å). In contrast, yttrium cations of $[Y(dmf)_8][Cu_4(\mu_3\text{-}I)_2(\mu\text{-}I)_3I_2]$ (**379**) and $[Y(dmso)_6(dmf)_2][CuI_3][I]$ (**380**) have a distorted dodecahedral stereochemistry [98,99]. The two dmf ligands in the mixed-ligand cation of **380**, situated in the *cis* position with the O–Y–O angle equal to 72.3(3)°, have average Y–O distance 2.38 Å, which is slightly longer than the Y–O (dmso) distance (av. 2.33 Å).

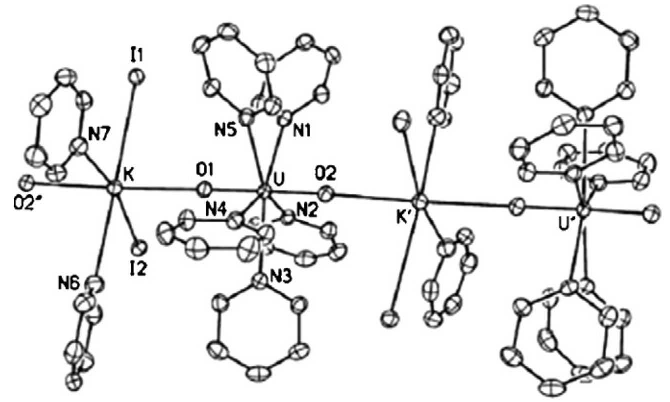
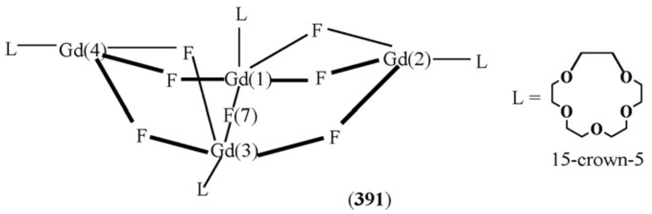


Fig. 13. Structure of $\{[UO_2(py)_5][KI_2(py)_2]\}_\infty$ (**381**). Reproduced from Ref. [100] by permission of the Royal Chemical Society.



(**391**)

Fig. 14. Structure of $[Gd_4F_7(15\text{-crown-}5)_4]^{5+}$ cation of (**391**).

The structure of $\{[UO_2(py)_5][KI_2(py)_2]\}_\infty$ (**381**) [100] consists of *trans* dioxo linear $[UO_2]^+$ cations, surrounded in the equatorial plane by five pyridine ligands, and linked by the oxo groups with $[KI_2(py)_2]^-$ anionic fragments (Fig. 13). The two groups of atoms U, N1, N2, N3, N4, N5 and K, I1, I2, N6, N7 define two planes, which are almost parallel, with a dihedral angle of 4.28(7)°. The polymeric structure of **381**, which forms an infinite chain, is ensured by cation–cation interactions. These are now well documented in uranyl(VI) and neptunyl(V) chemistry and reflect the pronounced Lewis basicity of the axial oxygen atoms of the $[UO_2]^+$ moiety, which is related to the nature and number of the equatorial ligands.

The above ionic species **360–380** are attractive precursors to anhydrous hetrometallic macrocyclic complexes by direct ligand exchange of the loosely bound monodentate ligands of the cation with crown ether ligands [101–108]. The geometry of the cations in $[ScCl_2(\eta^5\text{-15-crown-5})]_2[CuCl_4]$ (**382**) [101], $[ScCl_2(\eta^5\text{-15-crown-5})][SbCl_6]$ (**383**) [102], $[ScCl_2(\eta^5\text{-benzo-15-crown-5})][SbCl_6]$ (**384**) [102] and $[ScCl(\eta^5\text{-15-crown-5})(MeCN)][SbCl_6]_2\cdot MeCN$ (**385**) [103] is *trans* pentagonal bipyramidal, which features a linear $ScCl_2$ unit [a ScCl(MeCN) unit in the case of **385**] inserted directly into the crown cavity and reflecting total involvement of the oxacrown oxygen atoms. As expected, the Sc–Cl bond is slightly shorter in the dication of **385** [2.361(2) Å] [103] than in the monocation of **382** and **384** [2.394(2)–2.427(8) Å] [101,102]. This preference of scandium for seven-coordinate pentagonal bipyramidal geometry featuring a threaded $ScCl_2$ unit and an equatorial array of five ring oxygen atoms continues for the larger crowns. So the $[ScCl_2(\eta^5\text{-18-crown-6})]^+$ cation in $[ScCl_2(\eta^5\text{-18-crown-6})][FeCl_4]$ (**388**) [103] and $[ScCl_2(\eta^5\text{-18-crown-6})][SbCl_6]$ (**389**) [106] has only five of the crown oxygen atoms bonded directly to scandium [Sc–O = 2.190(5)–2.264(2) Å], leaving the sixth and remaining ring oxygen well outside the equatorial ScO_5 plane and not involved in the metal coordination [Sc···O = 4.137(5) Å]. On the other hand, the gadolinium atom in $[GdCl_2(\eta^6\text{-dibenzo-18-crown-6})(MeCN)][SbCl_6]\cdot 2MeCN$ (**390**) is bonded to all the six oxygen atoms [2.545(4)–2.683(4) Å] of the oxacrown, one MeCN molecule [2.579(5) Å] and two *trans* chloride ions to give a nine-coordinate crown species, the geometry of which can best be described as capped hexagonal planar [107]. Similar structure was found for homometallic gadolinium-crown ether complexe **199** [183]. The two benzene rings of the crown fold over towards what is clearly the more sterically occupied side of the ring (i.e. the side having one chloride and MeCN ligands), resulting into non-equivalence of the gadolinium-chlorine bond distances [2.632(2) and 2.679(2) Å]. The $SbCl_6$ anions have a regular octahedral geometry with Sb–Cl bonds in the region 2.361(2)–2.386(2) Å.

Total halide abstraction from $ScCl_3$ by judicious use of $SbCl_5$ in tandem with $SbCl_3$ in acetonitrile solution in the presence of 12-crown-4 results in the formation of $[Sc(\eta^4\text{-12-crown-4})_2][SbCl_6][Sb_2Cl_8(MeCN)_2]\cdot 2MeCN$ (**386**) [104]. The Sc^{3+} cation is sandwiched by two crown ether ligands, each providing four oxygen donor sites, and assumes distorted square antiprismatic geometry [Sc-O = 2.160(8)–2.274(9) Å]. The two crown rings are essentially parallel and adopt a staggered conformation to minimise interligand repulsions. The accompanying centrosymmetric chloride-bridged counter anion $[Sb_2Cl_8(MeCN)_2]^{2-}$ represents a rare example of a discrete dimeric $[SbCl_4]_2$ structural unit, where the presence of coordinated acetonitrile ligands presumably blocks any further oligomerisation [104]. In contrast, the larger erbium accepts an acetonitrile ligand also in $[Er(\eta^4\text{-12-crown-4})_2(MeCN)][SbCl_6]_3$ (**387**) [105] and thus have a monocapped square antiprism environment. The planes of the two crown rings intersect at an angle of 73.0(1)°.

The unprecedented structure of $[Gd_4F_7(15\text{-crown-}5)_4][AsF_6]_5\cdot 6SO_2$ (**391**) is the first report of a $Ln_4(halide)_7{}^{5+}$ complex, which consists of a tetranuclear bowl with bridging fluoride ligands and four capping 15-crown-5 molecules (Fig. 14), together with $AsF_6{}^-$ counter-ions and lattice SO_2 molecules [108]. There are two separate environments for the four-gadolinium centres. Gd(1) and Gd(3) are nine-coordinate with five sites occupied by the oxygen atoms of the crown ether, and four by bridging fluorides, whereas Gd(2) and Gd(4) are eight-coordinate with a pentadentate crown ether and three bridging fluorides. The cluster comprises a puckered eight-membered ring with single fluoride bridges connecting Gd(1) to Gd(4) and Gd(2) to Gd(3). Double fluoride bridges join Gd(1) with Gd(2) and Gd(3) with Gd(4). Additionally, F(7) links transannular Gd(1) and Gd(3) leading to nine coordination, whereas there is no corresponding bridge between eight-coordinate Gd(2) and Gd(4). The best fit polyhedra for the coordination geometries of Gd(1), Gd(3) and Gd(2,4) are a tricapped trigonal prism, a doubled trigonal prism and a bicapped trigonal prism, respectively. Capping of the framework by the four crown ethers inhibits polymerization by lanthanoid–fluoride bridging. The lattice hosts five octahedral AsF_6^- units to provide charge balance, uncoordinated SO_2 molecules occupying the remainder of the voids in the lattice [108].

4. Luminescent properties

Lanthanide complexes, because of their unique coordination chemistry and intense luminescence with long excited-state lifetimes, are ideal materials for sensor applications. Surprisingly, relatively fewer reports on luminescent properties of lanthanide halide complexes with neutral O- or N-donor ligands have appeared in the literature [154,162,165,254–256]. This is despite the fact that some of these complexes are brilliant luminescent materials. For example, the complex $[Tb(antipyrine)_6]I_3$ (**137**) [154] shows magnificient triboluminescence, a property whereby a crystalline solid substance emits light upon fracture. The europium complex $[EuCl_3(\eta^2\text{-bipyO}_2)(MeOH)_2]$ (**168**) [162] is another example where fluorescence arises from intramolecular energy transfer from the ligand to the Eu^{3+} center. The absorption of UV radiation by the $bipyO_2$ ligand produces an excited triplet state, which in turn causes an intramolecular energy transfer to the Eu^{3+} ion. Upon decay from the excited state, fluorescence is observed. The absorption spectra are dominated by a strong band in the far UV region due to a IL $\sigma \rightarrow \sigma^*$ transition. The complex also exhibits a shoulder at *ca.* 294 nm, assigned as oxygen-to-metal charge transfer. Excitation of the complex at the absorption maximum = 285 nm causes a weak to strong emission at 293 K, assigned to ligand-to-metal charge transfer (LMCT).

Lanthanide halide compounds of the type $[Ln(\eta^4\text{-L})X_3]$, in which three halide anions are directly coordinated with Ln^{3+} center together with four nitrogen atoms of the ligand, has outstanding features as an anion-specific luminescent receptor; three ligand chromophores are well arranged to act as effective photon antenna; and several vacant sites of the lanthanide coordination sphere are available for incoming anion guests [197]. A representative example $[Tb(\eta^4\text{-tpa})X_3]$ [254] shows maximum luminescence intensity for chloride anion at 548 nm. On replacing chloride anions with nitrate or acetate anions, this intensity diminishes. Iodide and fluoride, on the other hand, completely suppresses this luminescenc [254]. Recently, a few reports have described luminescent properties of lanthanide iodides in ionic liquid medium [255].

5. Reactivity

The reductive chemistry of divalent lanthanides has seen an unprecedented growth in past two decades, mainly because of availability of stable, suitable, and relatively easy to handle Ln(II) iodide precursors with ligands such as thf, hmpa, dme, etc. [257]. However, in view of availability of excellent reviews on their catalytic activities and reactivity [13–15] as well as the fact that present review focuses mainly on synthesis and structural aspects, further discussions on the reactivities of Ln(II) halide complexes are omitted here. Some common but important reactions of homo- and heterometallic Ln(III) and An(III) halide complexes are discussed.

5.1. Oxidation and hydrolysis reactions

5.1.1. Homometallic complexes

Many of these compounds are air- and moisture-sensitive in view of highly oxophilic nature of lanthanides/actinides and also due to the fact that these metals have tendency to attain higher coordination numbers. For example, activation of dioxygen by the $YI_3(Pr^iOH)_4$ gives a unique yttrium superoxide $[Y_2I_2(\mu_2,\mu_0{:}\eta^1\text{-}O_2)_2(Pr^iOH)_8]I_2$ [258] (Fig. 15). This is the first structurally characterized yttrium superoxide as well as the first superoxide derived from an iodide. This type of bridging $\mu_2,\mu_0{:}\eta^1$ bonding mode of O_2 is hitherto unknown in lanthanide and transition metal chemistry. The O–O distance, 1.40(5) Å, in the bridging superoxide ligands and the Y–O–O angle, 123.1(9)°, are quite close to the calculated values of 1.33 Å and ca. 120°, respectively, for an end-on bonded superoxide ligand [258]. The DFT calculations indicate that this molecule is stable in its high spin triplet state with the SOMO-LUMO gap being 3.7 eV.

The tetranuclear peroxo complexes $[Ln_4(O_2)_2Cl_8(py)_{10}]\cdot py$ (Ln = Sm, Eu, Gd) are formed by action of atmospheric oxygen on heated pyridine solutions of the $[LnCl_3(daa)_2]$ [259].

$$4[LnCl_3(daa)_2] + 11py + 2O_2 \rightarrow [Ln_4(O_2)_2Cl_8(py)_{10}]\cdot py + 2Cl_2 + 8\,daa \quad (5)$$

In the X-ray structures of $[Ln_4(O_2)_2Cl_8(py)_{10}]$ (Ln = Sm, Eu, Gd), the four lanthanide atoms in coplanar array are linked *via* the two peroxo groups in a hitherto unobserved $\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2$ coordination (Fig. 16). Additionally, they are bonded by four μ-chloro bridges. Two of the Ln atoms complete their coordination sphere by three pyridine molecules each, the other two by two chlorine atoms and two pyridine molecules.

The reactions of yttrium triiodide isopropanolate, $YI_3(Pr^iOH)_4$ with stoichiometric amounts of water in the presence of di-, tri- and tetraglyme yield a facile synthetic route to hydroxo-bridged, centro-symmetric dimeric yttrium complexes [260]. The obtained ionic derivatives, $[Y_2(\mu\text{-OH})_2(H_2O)_2(EtOH)_4(\eta^3\text{-diglyme})_2][I]_4\cdot 2EtOH$, $[Y_2(\mu\text{-OH})_2(H_2O)_4(\eta^4\text{-triglyme})_2][I]_4\cdot 2EtOH$ and $[Y_2(\mu\text{-OH})_2(H_2O)_2(EtOH)_2(\eta^4\text{-tetraglyme})_2][I]_4$ contain a centrosymmetric $Y_2(\mu\text{-OH})_2$ diamond core (Fig. 17) and all the iodide ions act as non-coordinating counter-anions. Although the yttrium centers in the above three structures are eight-coordinated, their stereochemistry is a distorted square antiprism, a slightly distorted dodecahedron and a bicapped trigonalprism, respectively [260]. A similar hydroxo-bridged dinuclear lanthanide complex, $[Ce(\eta^4\text{-tpa})(\mu\text{-OH})(MeCN)(H_2O)]_2I_4$ containg N-donor ligands (tpa and MeCN) has also been reported by the addition of two equiv of H_2O to a solution of $[Ce(\eta^4\text{-tpa})_2]I_3$ in anhydrous acetonitrile [198]. These di-nuclear compounds are potentially good starting materials for the synthesis of larger yttrium and lanthanide oxo/hydroxo clusters.

Trace amounts of oxygen and water leads to the oxidation of the $[UI_2(\eta^3\text{-terpy})_2(py)]I$ complex to the U(IV) trinuclear μ-oxo species $[\{UI(\eta^3\text{-terpy})_2(\mu\text{-O})\}_2\{UI_2(\eta^3\text{-terpy})\}]I_4$, which con-

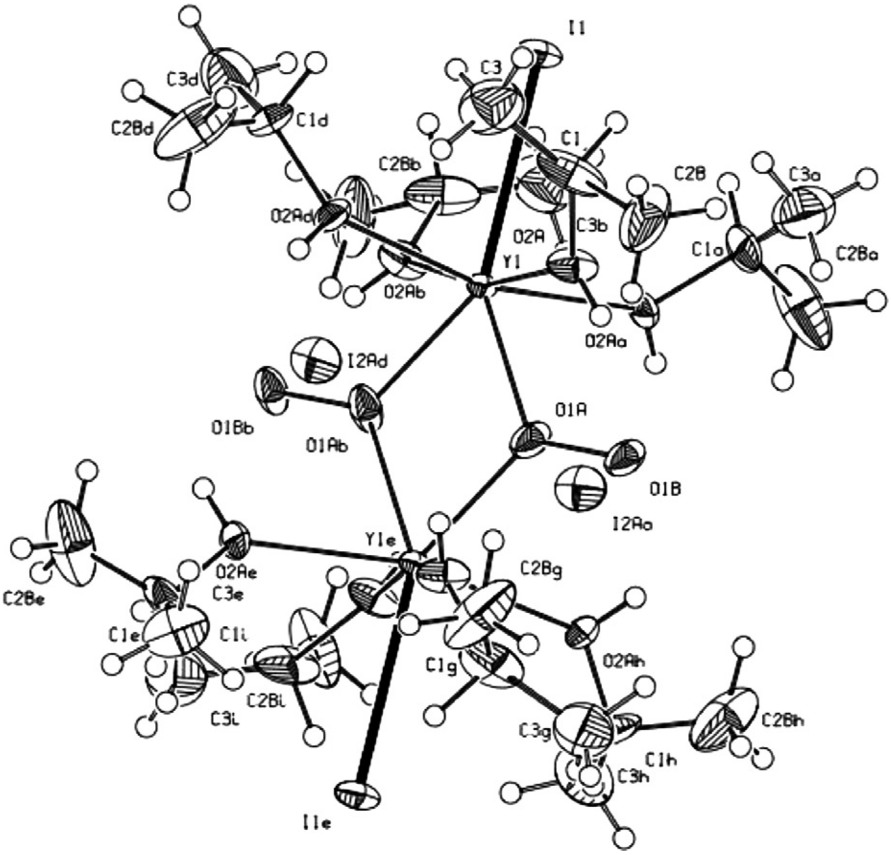


Fig. 15. Structure of $[Y_2I_2(\mu_2,\mu_0{:}\eta^1\text{-}O_2)_2(Pr^iOH)_8]I_2$ [258].

tains two μ-oxo bridges between the three uranium cations. The most striking feature of this complex is the linear arrangement of the cations, with U–O–U angles ranging from 158 to 173° [261]. In analogy to the U–terpy complex, the U–tpa complex is also reactive towards oxidation and hydrolysis. For instance, reaction of $[U(\eta^4\text{-tpa})_2]I_3$ with trace amounts of H_2O/O_2 in acetonitrile led to the formation of the corresponding U(IV) hydroxo complex, $[U(\eta^4\text{-tpa})_2(OH)_2]I_2{\cdot}3MeCN$. In this complex, the metal is 10-coordinate with the iodide anions not being formally coordinated [200]. Attempts at forming this complex by reacting the starting U(III) species with oxygen-free water in acetonitrile produced the trinuclear complex, $\{[U(\eta^4\text{-tpa})(\mu\text{-}O)I]_3(\mu_3\text{-}I)\}{\cdot}3MeCN$. Intriguing aspects of this structure include the six-membered ring created by the uranium cations and the 3μ-oxo atoms, as well as the bridging iodide atom which coordinates all three uranium centers [200]. The *mono-* and *bis*-methoxo U(IV) complexes, $[U(\eta^4\text{-tpa})I_3(OMe)]$ and $[U(\eta^4\text{-tpa})I_2(OMe)_2]$, have also been isolated when various amounts of methanol were added to an acetonitrile solution containing tpa and $UI_3(thf)_4$. It was postulated that oxidation of the uranium cation is facilitated through formation of methoxide anion and subsequent coordination to the uranium center [200]. It has also been suggested that the synthesis of $UI_2(OPr^i)_2(HOPr^i)_2$ from uranium metal, iodine and isopropanol involves the production of an intermediate such as $UI_4(HOPr^i)_x$, which then eliminates HI to form the final uranium iodoalkoxide product [73].

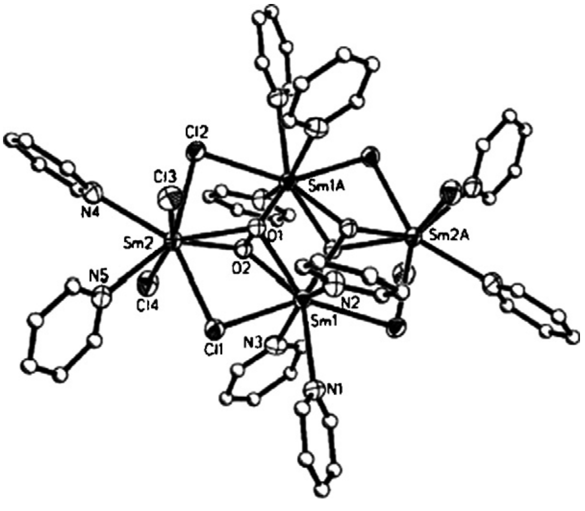


Fig. 16. Structure of $[Sm_4(\mu^3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}O_2)_2Cl_8(py)_{10}]$. Reproduced from Ref. [259] by permission of the Wiley–VCH.

5.1.2. Heterometallic complexes

The yttrium(III)–copper(I) heterometallic iodide compounds $[Y(dmf)_8][Cu_4I_7]$ (**379**) and $[Y(dmso)_6(dmf)_2][CuI_3][I]$ (**380**) undergo unique crystal-to-crystal transformations *via* progressive substitution of dmf ligands by water molecules in a confined, solvent-free environment [98,99]. Partial substitution of the dmf ligands of the $[Y(dmf)_8]^{3+}$ cation of **379** by water in paratone after 1 week afforded a mixed-ligand cation

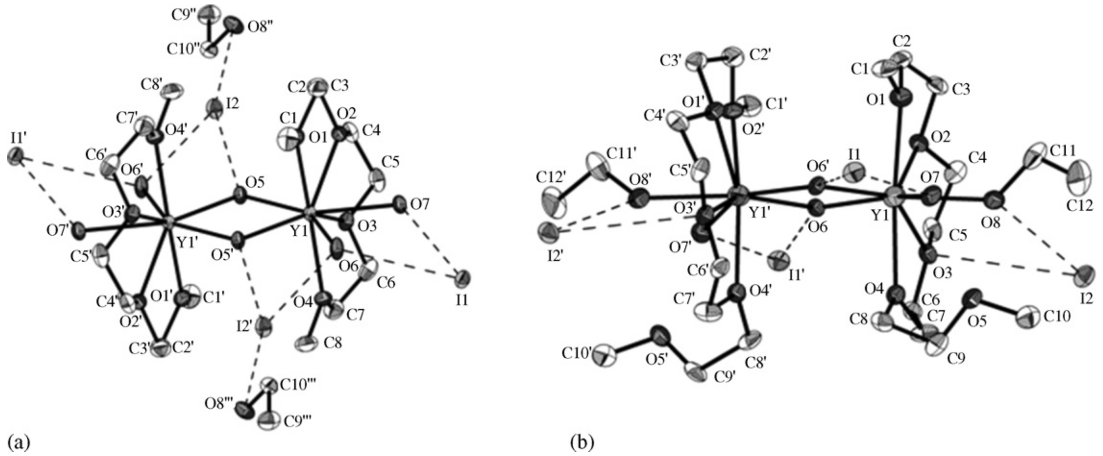
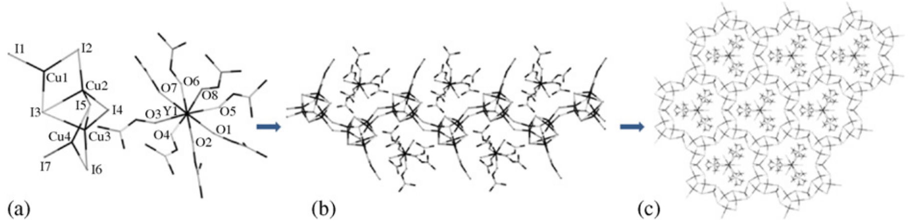


Fig. 17. Structures of (a) $[Y_2(\mu\text{-}OH)_2(H_2O)_4(\eta^4\text{-triglyme})_2][I]_4\cdot 2EtOH$ and (b) $[Y_2(\mu\text{-}OH)_2(H_2O)_2\text{-}(EtOH)_2(\eta^4\text{-tetraglyme})_2][I]_4$ [260].



Scheme 10. Gradual transformations of the ion-pair $[Y(dmf)_8][Cu_4I_7]$ (a) into extended arrays $[Y(dmf)_6(H_2O)_2]^{3+}[Cu_7I_{10}]_{1\infty}{}^{3-}$ (b) and $[Y(dmf)_6(H_2O)_3]^{3+}[Cu^I{}_7Cu^{II}{}_2I_{14}]_{2\infty}{}^{3-}$ (c) by H-bond templating in paratone over 1 or 2 weeks, respectively [99].

$[Y(dmf)_6(H_2O)_2]^{3+}$ where the metal has a dodecahedral stereochemistry. The change in the cation leads to a change of its counter ion giving compound $[Y(dmf)_6(H_2O)_2]^{3+}[Cu_7(\mu_4\text{-}I)_3(\mu_3\text{-}I)_2(\mu\text{-}I)_4(I)]_{1\infty}{}^{3-}$ (Scheme 10). The initial tetranuclear $[Cu_4(\mu_3\text{-}I)_2(\mu\text{-}I)_3I_2]^{3-}$ clusters in **379** are transformed into heptanuclear $[Cu_7(\mu_4\text{-}I)_3(\mu_3\text{-}I)_2(\mu\text{-}I_4)(I)]^{3-}$ units associated into zig–zag chains [angle 62.2(3)°] *via* bridging iodide ions. The yttrium cations occupy alternate positions along the Cu–I chain and the overall structure of compound $[Y(dmf)_6(H_2O)_2]^{3+}[Cu_7(\mu_4\text{-}I)_3(\mu_3\text{-}I)_2(\mu\text{-}I)_4(I)]_{1\infty}{}^{3-}$ is a 1D polymer. The presence of two water molecules on the cation introduces bi- and tetra-furcated H-bonding with I···O (H_2O) distances ranging from 3.59(2) to 3.88(2) Å [99]. Further introduction of water into the coordination sphere of yttrium of $[Y(dmf)_6(H_2O)_2]^{3+}[Cu_7(\mu_4\text{-}I)_3(\mu_3\text{-}I)_2(\mu\text{-}I)_4(I)]_{1\infty}{}^{3-}$ in paratone after 1 week afforded the $[Y(dmf)_6(H_2O)_3]^{3+}$ cation (Scheme 10), where the metal is nine-coordinated with a tricapped trigonal prismatic geometry. The six oxygen atoms of the dmf ligands are located at the corners of the prism whereas those of the water ligands cap the tetragonal faces in a quite symmetric trigonal planar arrangement around yttrium. The presence of additional water ligand and thus change in geometry of the cation leads to subsequent condensation of the copper iodide cluster. Another observation is the formation of a mixed-valence copper iodide building block $[Cu^I{}_7Cu^{II}{}_2(\mu_3\text{-}I)_8(\mu\text{-}I)_6]^{3-}$ as confirmed by ESR. Each water molecule of the cation is involved in bifurcated H-bonding [av. I···O (H_2O) = 3.52 Å] with iodide ions allowing thus the assembly of three building block $[Cu_9I_{14}]^{3-}$ units to form a ring [radius 5.28(5) Å] due to the 120° angle between the water molecules of the cation, which is encapsulated. There are six neighboring rings around each ring and thus a 2D sheet-like structure is obtained (Scheme 10) [99].

Substitution of two dmf ligands of the $[Y(dmso)_6(dmf)_2]^{3+}$ cation in **380** by water affords a mixed-ligand cation $[Y(dmso)_6(H_2O)_2]^{3+}$ where square antiprism geometry of the metal is slightly distorted towards bicapped trigonal prismatic geometry. Although, the change in the cation does not lead to a change of its counter anions in $[Y(dmso)_6(H_2O)_2][CuI_3][I]$, presence of water molecules introduces H-bonding between I···O (water) [I···O = 3.417(8)–3.570(8) Å], which brings $[CuI_3]^{2-}$ anion closer to yttrium cation [Y···Cu distance 7.050(2) Å in $[Y(dmso)_6(H_2O)_2][CuI_3][I]$ versus 7.586(2) Å in **380**]. The other anion I^- is also closer in mixed ligand H_2O–dmso complex [5.962(2) Å] than in **380** [6.523(2) Å]. It is interesting to note that simply by choosing between dmso or dmf in the cation $[Y(L)_6(H_2O)_2]^{3+}$ (L = dmso or dmf) two very different structures, a 1D polymer $[Y(dmf)_6(H_2O)_2]^{3+}[Cu_7(\mu_4\text{-}I)_3(\mu_3\text{-}I)_2(\mu\text{-}I)_4(I)]_{1\infty}{}^{3-}$ and an ion-pair $[Y(dmso)_6(H_2O)_2][CuI_3][I]$, are obtained [98].

5.2. Miscellaneous reactions

Dissolution of $[LuI_2(Pr^iOH)_4][I]$ (**82**) in pyridine generates an unexpected mixed iodo-alkoxide species, $[LuI(OPr^i)(py)_5][I]$, by a reaction which likely involves the elimination of HI [43]. The formed mixed iodo-alkoxide complex exhibits an ionic structure similar to that of $[LuI_2(py)_5][I]$ (**213**) [43] with a $[LuI(OPr^i)(py)_5]$ cation and a naked iodine anion. Photolysis of $[YbI_2(\eta^2\text{-dme})_2(\eta^1\text{-dme})]$ (**21**) in sunlight produces a methoxo-bridged dimeric species $[YbI_2(\mu\text{-OMe})(\eta^2\text{-dme})]_2$ [262]. The elimination of ethene during the reaction was confirmed by ^{1}H NMR spectroscopy. A new type of acetonitrile compound of lanthanide(III) iodide $[\{(HN{=}CMe)_2MeCNH_2\}Ln(MeCN)_6]I_3$ (Ln = Dy (**219**), Tm (**220**) [186]) was reported to form on dissolving TmI_2 and DyI_2 in acetonitrile, which accompanied by disproportionation of the salt and its interaction with the solvent leading to formation of C–C bonds

$$3LnI_2 \underset{Ln=Dy(\mathbf{219}),Tm(\mathbf{220})}{\xrightarrow{MeCN}} [\{(HN = CMe)_2MeCNH_2\}Ln(MeN)_6]I_3$$

$$+LnI_3(MeCN)_8 + [LnI(RR')] \qquad (6)$$

In the structure of **219** and **220**, the metal is coordinated not only to six molecules of acetonitrile but also to a new tridentate ligand 2,4-diimino-3-methyl-3-aminopentane. The compound $[UI_4(MeCN)_4]$ undergoes ring-opening in thf; the product has been isolated as the adduct $[UI_2(OCH_2CH_2CH_2CH_2I)_2(OPPh_3)_2]$ [263].

6. Conclusions and looking ahead

In this review article, an attempt has been made to present collectively the different aspects of anhydrous scandium, yttrium, lanthanide and actinide halide complexes with neutral oxygen and nitrogen-donor ligands. These complexes, especially with simple donor ligands such as tetrahydrofuran, isopropanol, pyridine and dimethoxyethane remain the most important starting materials for the synthesis of lanthanide and organolanthanide(actinide) complexes. The coordination chemistry of different oxygen and/or nitrogen donor ligands with lanthanide halides is very exciting and several structurally diverse metal complexes have been synthesized and structurally characterized. These structural data constitute a fundamental basis for the understanding of the role that a donor ligand plays in lanthanide halide-catalyzed reactions. Moreover, an awesome development in the reductive chemistry of Sm(II), Eu(II) and Yb(II) has been possible because of availability of stable, suitable, and relatively easy to handle Ln(II) iodide precursors with thf, hmpa, dme, etc. The recent discoveries of stable and isolable Tm(II), Dy(II) and Nd(II) iodide adducts with thf and/or dme ligands are proving to be boon for LnI_2-promoted reactions. Furthermore, potentially multidentate N-donor ligands have been shown to bind uranium(III) and other actinide halides preferentially over lanthanide(III) halides, where halide anions influence the selectivity. This preferencial affinity finds potential applications in selective extraction of trivalent actinides in the nuclear wastes and separates them from the trivalent lanthanides. Recent advances in these lanthanide halide complexes include their use as precursors in designing and synthesizing heterometallic derivatives by halide abstraction method.

In spite of the exciting and interesting advancements in the syntheses, structural characterization and catalytic applications in organic reactions, some areas still remain to be explored further. The utility of these compounds as promising sensory materials is clearly one of those areas. In view of interesting luminescent and scintillation properties, some of these compounds are promising candidates for it and further research is needed to establish it concretely. Another area which requires more attention is the utility of these lanthanide halide derivatives as synthons for the synthesis of polymetallic assemblies. Inspite of some advancement in this field (Section 3.4), designing and generating robust supramolecular networks using these lanthanide halide complexes as precursors has remained largely unexplored. Owing to their versatile bonding modes, iodide anion has potential to play important role in generating iodide-mediated supramolecur frameworks. Some efforts in this regard have been started recently and it is anticipated that future research will prove rewarding in this area.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ccr.2007.10.029.

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