Scandium, yttrium, the lanthanides

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This chapter reviews the literature reported during 2012 on scandium, yttrium and the lanthanide elements.

Highlights

Highlights include the first molecular complexes of holmium and erbium in the +2 oxidation state, as well as the first molecular SO_2 complexes of the lanthanides.

Introduction

There continues to be an increasing amount of research in this area, and it has not been possible to cite all interesting research published in 2012. A new book covering many aspects of the chemistry of these elements has appeared.[1] There is continued concern that demand for these elements could outstrip supply.[2,3] Whilst gadolinium-based MRI agents are the most obvious application of lanthanides in medicine, less obvious applications include the ability of lanthanum oxide nanoparticles to scavenge phosphate and thus kill microorganisms[4] and cerium oxide nanoparticles protecting against ischemic stroke by scavenging reactive oxygen species.[5]

Reviews have appeared of such areas as lanthanide (and actinide) hydration,[6] compounds with metal–metal bonds between lanthanides and other metals,[7] recent developments in the coordination chemistry of europium(II),[8] thermo-dynamics of lanthanide(III) complexation in non-aqueous solvents,[9] shape-controlled synthesis and catalytic application of ceria nanomaterials[10] and lanthanide amidinates and guanidinates.[11] Two surveys cover applications in organic chemistry, selective reductions using samarium diiodide–water[12] and other Ln(II) reducing agents.[13] Surveys of the organometallic chemistry of the lanthanides for both 2009 and 2010 have appeared.[14,15] Reviews directed towards spectroscopy cover porphyrin lanthanide complexes for NIR emission,[16] luminescent lanthanide-containing metallopolymers,[17] charge transfer excited states sensitization of lanthanide emitting from the visible to the near-infra-red,[18] Gd-DTPA derivatives as MRI contrast agents,[19] MRI probes for

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cellular labeling,[20] and lanthanide complexes as chiral probes in circularly polarized luminescence.[21] A review[22] on lanthanides in molecular magnetism is timely, whilst their role in magnetic refrigeration has also been surveyed.[23]

Scandium

Ab initio simulations suggest either pentagonal bipyramidal or trigonal prismatic structures for the $[Sc(H_2O)_7]^{3+}$ aqua ion.[24] Volatile guanidinate-derived complexes $[M(DPDMG)_3]$ (M = Sc, Y, Er) have been synthesised as precursors for synthesis of oxide thin forms by MOCVD; all are six coordinate.[25] Scandium zeolite complexes have been reported to be efficient recyclable heterogeneous catalysts for imino-Diels–Alder reactions.[26] Scandium imide complexes continue to be of interest. In the presence of pyridine, $[(PNP)Sc(NH(DIPP))(CH_3)]$ eliminates methane forming first the transient $[(PNP)Sc=N(DIPP)(NC_5H_5)]$, which then activates the C–H bond of pyridine in 1,2-addition fashion generating the pyridyl complex $[(PNP)Sc(NH(DIPP))(\eta^2\text{-}NC_5H_4)]$.[27] A cyclopentadienylphosphazene-based scandium imide induces intramolecular C–H bond activation at room temperature.[28] Other terminal imides form heterobimetallic complexes with halides of transition metals which have greater catalytic ability than the starting materials.[29]

A comparison of the borohydrides $[(C_5Me_4H)_2Ln(THF)(BH_4)]$ and $[Cp*_2Ln(THF)(BH_4)]$ (Ln = Sc, Y) with the established $[(C_5Me_4H)_2Ln][BPh_4]$ and $[Cp*_2Ln][BPh_4]$ indicates a preference for BH_4 bonding over BPh_4, and that the borohydrides are less suitable precursors in the reduction of dinitrogen.[30] Two β-diketiminato-supported scandium alkyls $[(\kappa^2\text{-}ArNC(^tBu)CHC(^tBu)NAr)ScR_2]$ (Ar = 2,6-$^iPr_2C_6H_3$; R = CH_3, CH_2SiMe_3) give mono- and bis(carboxylato) insertion products with CO_2.[31] The alkyls $[M(CH_2SiMe_3)_3(THF)_2]$ (M = Sc, Y) are synthons for phosphinoamide complexes, with yttrium affording mixed products, but scandium solely $[(ArNP^iPr_2)_2Sc(CH_2SiMe_3)(THF)]$ (Ar = 3,5-dimethylphenyl).[32] $[M(CH_2SiMe_3)_3(THF)_2]$ (M = Sc, Y, Lu) were also used as starting materials for alkyls and allyls supported by linked N-type functionalized cyclopentadienyl and fluorenyl ligands. A scandium allyl affords perfectly syndiotactic polystyrene.[33] The silylamide $[Sc(N(SiHMe_2)_2)_3(THF)]$ reacts with the amidine $[PhC(N-2,6-^iPr_2C_6H_3)_2]H$ forming a mono(amidinate) complex $[(PhC(N-2,6-^iPr_2C_6H_3)_2)Sc(N(SiHMe_2)_2)_2]$; when activated, this acts as an isoprene polymerization catalyst.[34] Scandium and yttrium arene inverse-sandwich complexes of naphthalene and anthracene react with white phosphorus forming compounds containing P_8^{4-} and P_7^{3-} units.[35] Mechanisms have been advanced for the *ortho* alkylation of pyridines *via* C–H addition to olefins by cationic half-sandwich scandium alkyl species.[36] Although $[Cp*_2Sc]^+ [HB(p\text{-}C_6F_4R)_3]^-$ (R = F, H) are unreactive towards D_2 or α-olefins, they react with CO *via* an isocarbonyl linkage.[37]

Simple compounds and complexes of the lanthanides

$Y_8S_{14.8}$, $Tb_8S_{14.8}$, $Dy_8S_{14.9}$, and $Ho_8S_{14.9}$ have the Gd_8Se_{15} type structure, containing S^{2-} and dinuclear S_2^{2-} anions.[38] Thermolysis of the dithiocarbamate complex $[Gd(S_2CN(C_4H_8)]_3\cdot phen]$ at *ca.* 350 °C in the presence of sulfur vapour yields pure γ-Gd_2S_3.[39] Solutions of SmI_2 in THF are widely used in the Barbier reaction. A rapid electrosynthesis using oxidation of a samarium rod provides THF solutions with a

greater SmI_2 concentration than hitherto available.[40] Two investigations have been reported of the Ce^{4+} aqua ion. A molecular dynamics simulation was based on a $[Ce(H_2O)_9]^{4+}$ ion,[41] but a detailed EXAFS study, backed by DFT calculations, favours an oxo-bridged dimer,[42] in contrast to that for Th, U and Np. A number of alcohol complexes of cerium(III) halides such as $[(CeCl_3)_7(BuOH)_{16}(H_2O)_2]\cdot(BuOH)_2$, $[(CeCl_3)_7(PrOH)_{16}(H_2O)_2]\cdot(PrOH)_2$ and $[(CeBr_3)_7(PrOH)_{18}]\cdot(PrOH)_2$ have structures usually based on catenated tetradecanuclear rings.[43] Polyether complexes $[CeBr_2-(diglyme)_2]^+$ $[CeBr_4(diglyme)]^-$, $[CeBr_3(DME)_2]$ and $[CeBr_3(tetraglyme)]$ have been synthesized from $[CeBr_3(THF)_4]$[44] whilst monoglyme acts as a partitioning agent to displace water in the syntheses of $[Ln(hfac)_3(monoglyme)]$ (Ln = La, Ce, Pr, Sm, Eu, Gd, Tb, Dy, Er, Tm).[45]

2,6-Bis(benzimidazol-2-yl)pyridine ligands form nine-coordinate 1 : 1 adducts with $[Ln(hfac)_3]$ (Ln = La, Eu, Gd, Lu, Y), of which the Eu complex exhibits strong red photoluminescence.[46] Such adducts formed by β-diketonates are nowadays familiar. Using a triarylamine-functionalized terpyridine ligand enables the formation of an adduct which exhibits "ON–OFF" switchable luminescence upon oxidation/reduction of the triarylamine.[47] Using a bis-β-diketone ligand has permitted the synthesis of complexes with triple-stranded dinuclear structures, often strongly luminescent, $[Ln_2(BTB)_3(C_2H_5OH)_2(H_2O)_2]$ (Ln = Eu, Gd), $[Ln_2(BTB)_3(DME)_2]$ (Ln = Nd, Yb), $[Eu_2(BTB)_3L_2]$ (L = 2,2-bipy, phen, 4,7-diphenyl-1,10-phenanthroline).[48] Phosphine oxide complexes continue to interest. With Et_3PO, lighter lanthanides form 9 coordinate $[Ln(NO_3)_3(Et_3PO)_3]$ (Ln = La, Ce, Pr, Nd, Eu), whilst heavier metals give mixtures of $[Ln(NO_3)_3(Et_3PO)_3]$ and $[Ln(NO_3)_3(Et_3PO)_2]$;[49] in contrast, $^tBu_3PO$ gives 8 coordinate $[Ln(NO_3)_3(^tBu_3PO)_2]\cdot H_2O\cdot n EtOH$.[50] Tripodal phosphine oxide ligands $(OPR_2)_2CHCH_2POR_2$ (R = Ph, o-$CH_3C_6H_4$, p-$CH_3C_6H_4$, m-$(CH_3)_2C_6H_4$) generate nine coordinate yttrium complexes $[Y(NO_3)_3((OPR_2)_2CHCH_2POR_2)]$; complexes with mixed phosphine–phosphine oxide ligands have also been reported.[51] Complexes of the early lanthanides $[Ln(XPA)_2Cl_3(solv)_2]$, (Ln = La, Ce, Nd; solv = H_2O and CH_3OH) with a mixed phosphine oxide have been studied.[52] A number of dimeric pivalate complexes of terbium, $[Tb_2(piv)_6(Hpiv)_6]$, $[Tb_2(piv)_6L_2]$ (L = bipy, phen, bath), as well as $[Ln_2(piv)_6(bpy)_2]$ and $[Ln_2(piv)_6(phen)_2]$ (Ln = Eu, Gd) have been fully characterised.[53] ^1H and ^{13}C NMR measurements on $[Ln(18\text{-crown-}6)(NO_3)_3]$ (Ln = La, Ce, Pr, Nd) have been interpreted in terms of six-site proton exchange, with the paramagnetic compounds suggested as subnanoscale NMR spectroscopic probes for temperature measurement in non-aqueous media.[54]

Solvent free synthesis from the anhydrous trichlorides and 1,3-benzodinitrile leads to $_\infty^3[LnCl_3(1,3\text{-Ph}(CN)_2)]$ (Ln = Eu, Tb), which have luminescent 3D framework structures.[55] Solvothermal syntheses have again been used to synthesise complexes of amine ligands, including thiostannates $[Y_2(dien)_4(\mu\text{-OH})_2]Sn_2S_6$, $(tetaH)_2[Ln_2(teta)_2(tren)_2(\mu\text{-}Sn_2S_6)]Sn_2S_6$ (Ln = Eu, Sm) and $[Eu_2(tepa)_2(\mu\text{-OH})_2-(\mu\text{-}Sn_2S_6)](tepa)_{0.5}\cdot H_2O$,[56] and thioantimonates $[Sm_4(tepa)_4(\mu\text{-}\eta^2,\eta^3\text{-}Sb_3S_7)_2(\mu\text{-}Sb_2S_4)]$ and $[Eu_2(tepa)_2(\mu\text{-}SbS_3)(\mu\text{-OH})]_2(SbS_4)(OH)\cdot H_2O$.[57] Continuing the search for new extractants for the separation of lanthanides from actinides in nuclear waste, a tetradentate terpy-based ligand, $CyMe_4$-hemi-BTBP, forms 1 : 1 complexes with lanthanides, of which $[Ln(NO_3)_3(CyMe_4\text{-hemi-BTBP})]$ (Ln = Ce, Eu) have been shown to be 10 coordinate.[58] Studies of Eu(III) complexing by bis(triazinyl)bipyridines (BTBPs) in octan-1-ol reveals that the 2 : 1 complexes are the ones extracted, usually 9

coordinate. The double salt $[Eu(CyMe_4\text{-}BTBP)_2(NO_3)]^{2+}$ $[Eu(NO_3)_5]^{2-}$, in which nitrate groups are all bidentate, has been isolated; when recrystallized, it forms $[Eu(CyMe_4\text{-}BTBP)(NO_3)_3]$, with nine coordinate europium.[59] 2,6-Bis(5-(2,2-dimethyl-propyl)-1H-pyrazol-3-yl)pyridine gives a very good separation factor for Am(III) over Eu(III). Complexes $[Ln(C5\text{-}BPP)(NO_3)_3(DMF)]$ (Ln = Sm, Eu) have been isolated; they contain 10-coordinate metals, with three bidentate nitrates and a coordinated DMF.[60]

Within the area of ionic liquids, phosphine oxide functionalised ionic liquids have been synthesised as lanthanide complexing agents. A singular complex has been isolated in which a phosphine oxide is coordinated to the $[Eu(hfa)_4]^-$ ion, usually regarded as coordinatively saturated.[61] Of a number of low-melting complexes containing 12 coordinate $[Ln(dcnm)_6]^{3-}$ ions, $(C_2mim)_3[La(dcnm)_6]$ and $(C_2C_1mim)_3[Pr(dcnm)_6]$ are ionic liquids.[62] Rapid cooling of molten $(Bu_4N)_3[Ln(dcnm)_6]$ (Ln = La–Nd, Sm) leads to crystallisation of a kinetically trapped but thermodynamically less stable polymorph, with a lower melting point than the more thermodynamically stable polymorph.[63]

The hexadentate ligand $(^{tBu}ArOH)_3tacn$ so effectively encapsulates lanthanide ions in the complexes $[((^{tBu}ArOH)_3tacn)Ln]$ (Ln = Sm, Eu, Lu) that no THF solvent can coordinate. Whilst they are unreactive to CO, CO_2 or O_2, the Sm and Eu compounds change colour immediately on exposure to SO_2 (colourless or yellow to red-orange); this coordination of SO_2 is reversible. The adducts have dinuclear structures with the two lanthanides bridged by the SO_2 molecule, coordinated in the $\mu,\eta^1,\eta^1\text{-}O,O'$ mode. These are thus the first molecular SO_2 complexes of the lanthanides.[64]

Alkoxides and aryloxides, amides and borohydrides

Amongst borohydrides, the most interesting reports[65,66] concern very volatile N,N-dimethylaminodiboranate ($H_3BNMe_2BH_3$) complexes, potential CVD precursors for metal boride and oxide thin films. The adducts $[Ln(H_3BNMe_2BH_3)_3(THF)]$ are mainly 13-coordinate monomers (those of Tm, Yb, and Lu are 12 coordinate) but in the base-free $[Ln(H_3BNMe_2BH_3)_3]$ compounds the coordination numbers decreases from 14 (Pr) via 13 (Sm) to 12 (Dy, Y, Er). Straightforward syntheses have been reported for $[Ln(BH_4)_2(THF)_2]$ (Ln = Eu, Yb); the Eu compound shows a strong blue luminescence in the solid state.[67] Bis(β-diketiminate) borohydrides$[[(L^{2,6\text{-}ipr2}_{Ph})_2\text{-}LnBH_4]$ and $[(L^{2\text{-}Me})_2LnBH_4]$ (Ln = Y, Yb) are active catalysts in the ring-opening polymerization of L-lactide (L-LA) and ε-caprolactone.[68] $[Ln(BH_4)_3(THF)_n]$ (Ln = La, Ce, Sm, Yb), are catalysts for the polymerization of ε-caprolactone; the cerium compound has the structure $[Ce(BH_4)_2(THF)_5]$ $[Ce(BH_4)_4(THF)_2]$.[69]

Iodine-activated lanthanides react with 2,6-diisopropylphenol forming the phenoxides $[Ln(Odip)_3(thf)_n]$ (Ln = La, Nd, n = 3; Ln = Sm, Dy, Y, Yb, n = 2), $[Eu(Odip)(\mu\text{-}Odip)(thf)_2]_2$, $[Ln(Odip)_3(dme)_2]$ (Ln = La, Yb) and $[La(Odip)_3(dig)]$.[70] $[Ce(OTf)_3]$ and $[Ce(N(SiMe_3)_2)_3]$ have been used as starting materials for the syntheses of naphthoxide complexes including $[Li(py)_2]_3[Ce(naphO)_6]$ and $[Li(DME)]_4[Ce_2(naphO)_{10}]$; solution structures are solvent dependent.[71] The 1,1′-binolate framework in the complexes $[M_3(thf)_x][(binolate)_3Ce^{III}(thf)_y]$ (M = Li, Na, K) shifts the oxidation potential considerably, producing strong stabilisation of Ce^{IV};

complexes $[Li_3(thf)_5][(binolate)_3Ce^{IV}Cl]$ and $[M_2(thf)_n][(binolate)_3Ce^{IV}]$ (M = Na, K) were isolated.[72]

The species formed on reduction of $[Y(N(SiMe_3)_2)_3]$ continue to expand. On reduction by K, ethereal solutions of $[Y(N(SiMe_3)_2)_3]$ turn blue and react with CO forming $[(K_2(18\text{-crown-}6)_2)(((Me_3Si)_2N)_3Y(\mu\text{-CO})_2)]$, in which trigonal bipyramidal $[((Me_3Si)_2N)_3Y(\mu\text{-CO})_2]^{2-}$ ions are present.[73] A rich oxidation chemistry has been uncovered for the side-on bound $(N_2)^{2-}$, $(N_2)^{3-}$, and $(NO)^{2-}$ complexes of $[((Me_3Si)_2N)_2Y]^+$. Thus, $[(((Me_3Si)_2N)_2(THF)Y)_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)]$ reacts with O_2 forming the $(O_2)^{2-}$ bridging side-on peroxide $[((Me_3Si)_2N)_2(THF)Y]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}O_2)$. Oxidation of the dinitrogen complexes gives the $(\mu\text{-O})^{2-}$ oxide-bridged bimetallic complex, $[((Me_3Si)_2N)_2(THF)Y]_2(\mu\text{-O})$, as a byproduct. $[(((Me_3Si)_2N)_2(THF)Y)_2(\mu\text{-}\eta^2{:}\eta^2\text{-NO})]$ and $[(((Me_3Si)_2N)_2(THF)Y)_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)]$ both react with $AgBPh_4$ forming $[((Me_3Si)_2N)_2Y(THF)_3][BPh_4]$.[74] The THF ligand in dimeric $[(((Me_3Si)_2N)_2(THF)Y)_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)]$ is displaced by a number of Lewis bases forming $[(((Me_3Si)_2N)_2(L)Y)_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)]$ (L = PhCN, py, DMAP, Ph_3PO, Me_3NO).[75] The reaction of $[Y(N(SiMe_3)_2)_3]$ with $[Ph_3PMe]I$ leads to the yttrium phosphonium methylide complex $[Y\{N(SiMe_3)_2\}_2I(CH_2PPh_3)]$; this in turn reacts with benzophenone forming a betaine complex $[Y\{N(SiMe_3)_2\}_2I(OCPh_2CH_2PPh_3)]$.[76] This reacts with Ph_3PO forming 1,1-diphenylethene in very good yield. The Yb(II) silylamide $[(THF)_2Yb\{N(SiMe_3)_2\}_2]$ reacts with 1,3-diisopropyl-4,5-dimethyl-imidazol-2-ylidene (IiPr) and 1,3-bis(2,4,6-trimethylphenyl)-imidazol-2-ylidene (IMes) forming three coordinate carbene complexes $[(NHC)Yb\{N(SiMe_3)_2\}_2]$ which are effective catalysts for the cross-dehydrogenative coupling of silanes with amines.[77] Optical spectra of the four coordinate adducts $[Sm(N(SiMe_3)_2)_3(L)]$ (L = THF, Ph_3PO and $C_6H_{11}NC$) and the five coordinate (bis) adducts $[Sm(N(SiMe_3)_2)_3(L)_2]$ (L = THF, Ph_3PO) have been assigned.[78] A dianionic β-diketiminate ligand has been generated to support lanthanide amides in $[L'LnN(SiMe_3)_2(THF)]$ ($L' = (2,6\text{-}^iPr_2C_6H_3)NC(CH_2)\text{-}CHC(CH_3)N(2,6\text{-}^iPr_2C_6H_3)^{2-}$; Ln = Yb, Y, Gd, Sm); under the same reaction conditions, Nd only forms the compound of the "normal" monoamide, $[LNd(N(SiMe_3)_2)_2]$ (L = $((2,6\text{-}^iPr_2C_6H_3)NC(CH_3))_2CH^-$).[79] Reaction of $EuCl_3$ with the sodium salt of bulky β-diketiminates NaL gives Eu(II) compounds in a sterically induced reduction.[80]

Organometallics

$[Ln(CH_2SiMe_3)_3(thf)_2]$ continue to be popular synthons in organometallic chemistry, as in the synthesis of phosphazene-functionalized cyclopentadienyls (see also p. 2 and p. 3 of this MS).[81] Reduction of $[Cp'_3Ln]$ [Ln = Ho, Er] by KC_8 affords the first molecular complexes of holmium and erbium in the +2 oxidation state, $[(18\text{-crown-}6)K][Cp'_3Ln]$, analogous to the Y(II) species recently reported. DFT calculations suggest that the HOMOs are largely $5d_{z^2}$ in character.[82] The congested $[Ln(\eta^5\text{-Cp''})_3]$ (Ln = Y, Er, Yb) have all been characterised. Attempts to prepare the Sc analogue from $[ScCp''_2I(THF)]$ and KCp'' were unsuccessful. Reaction of $[ScCp''_2I]$ with $[K(18\text{-crown-}6)]_2[C_6H_2(SiMe_3)_4\text{-}1,2,4,5]$ gives the striking dimer $[(ScCp''_2)_2(\mu\text{-}\eta^2{:}\eta^2\text{-}C_2H_4)]$.[83] The tuck-over hydride $[Cp^*_2Y(\mu\text{-H})(\mu\text{-}CH_2C_5Me_4)YCp^*]$ reacts with PhSSPh, AgOTf, and Et_3NHBPh_4 to form $[Cp^*_2Y(\mu\text{-SPh})_2Cp^*_2Y]$, $[Cp^*_2Y(\mu\text{-OTf})_2\text{-}Cp^*_2Y]$ and $[Cp^*_2Y(\mu\text{-Ph})_2BPh_2]$ respectively. It can act as a two-electron reductant when the bridging hydride and the bridging $Y\text{–}CH_2$ group can combine to

together to form a Cp* ligand and donate two electrons. [Cp*$_2$Y(μ-H)(μ-CH$_2$C$_5$Me$_4$)-YCp*] reacts with trimethylsilylchloride forming the tuck-over chloride complex, [Cp*$_2$Y(μ-Cl)(μ-η^1:η^5-CH$_2$C$_5$Me$_4$)YCp*].[84] *meso*-[(EBI*)CeI(THF)] is the first ansa-permethylindenyl lanthanide complex.[85] Reaction of [Cp'''$_2$CeH] with CH$_3$O-SO$_2$CH$_3$ proceeds first by activation of a methyl group, forming [Cp'''$_2$CeCH$_2$-SO$_2$(OCH$_3$)], which in turn forms [Cp'''$_2$CeOCH$_3$]. Further extended reaction gives [Cp'''$_2$CeOSO$_2$CH$_3$] and CH$_3$OCH$_3$.[86] The μ_2-imide complexes [Ln(AlMe$_4$)-(μ_2-Nmes*)]$_x$ (mes* = 2,4,6-C$_6$ ^{t}Bu$_3$H$_2$-2,4,6; Ln = Y, La, Nd, Lu) have some interesting features, with very short Ln–N distances. There are particularly short La–arene interactions in comparison with La(μ-CH$_3$) bridge distances.[87]

Spectroscopic studies

Processes involved in luminescence and upconversion from Tm^{3+} in solution have been examined.[88] Chiral complexes of europium have been investigated as probes, using CD and CPL to monitor levels of acute proteins in serum.[89] The effect of increasing the number of bipy units upon the luminescence properties of cryptates of Eu and Tb have been examined.[90] The photoluminescence and CPL behaviour of D-facam adducts of Eu(III) ^{i}Pr-Pybox complexes have been reported,[91] whilst water-soluble complexes of a pybox-type ligand exhibit very strong luminescence.[92] The heterobimetallic complex [CsEu((+)-hfbc)$_4$] has an exceptionally high ratio of polarization *versus* total luminescence; the clue to its CPL behaviour lies in the dynamic coupling between the f–f transitions.[93] Under UV irradiation, the achiral [Eu(bda)$_2$]$^-$ produces intense CPL in aqueous solutions in the presence of (S)-2-pyrrolidone-5-carboxylic acid.[94] A self-assembled heptanuclear europium wheel[95] is the largest example of a chiral luminescent complex of Eu^{3+}. Formation of terpyridine complexes by Eu^{3+} is the last step in self-assembly of luminescent gels.[96] A Yb(III) macrocycle containing a two-photon antenna has been used to perform in-depth scanning laser microscopy imaging of thick tissues.[97]

Two-photon excitation of a pair of Ir/Ln dyads (Ln = Eu, Tb) provides Ir and Ln emission with different lifetimes, separable by time-gated detection.[98] A Eu^{3+} macrocycle with appended naphthalimide group displays blue, red and green emission from different sources, permitting overall white emission.[99] Lanthanide complexes are reported of a DTPA-type ligand with quinoline-bisamide sidearms, the quinoline sensitising near-IR emission in both solutions and solid form of the ytterbium, erbium and neodymium complexes.[100]

Grafting two Ln^{3+} ions with different properties, Gd^{3+} and Eu^{3+} or Tb^{3+}, onto a single SiO$_2$ nanoparticle generates a probe with both MRI and luminescent functionalities, demonstrated in mouse macrophage cells.[101] A ytterbium–cyclen complex and xylenol orange have been used to make near-IR emitting gold nanoparticles whose emission can be switched on or off as a function of the pH value.[102] Gold nanoparticles functionalized with Gd^{3+} chelates show several desirable properties for *in vivo* MRI applications,[103] whilst Gd^{3+} complexes of DTPA-conjugates linked to gold nanoparticles have been developed as blood-pool and targeting MRI contrast agents.[104] Water soluble, luminescent gold nanoparticles with a luminescent Eu co-coating have been successfully introduced[105] into human platelets. Gd^{3+} ions bound to organic monolayers coating gold nanoparticles give information

on the monolayer organization.[106] $Fe_3O_4@LaF_3$:Yb^{3+}, Er^{3+} mesoparticles are potentially dual-modal magnetic/upconversion luminescence agents.[107]

An alanine derivative of Gd(DOTA) has been investigated as a high field, high relaxivity contrast agent,[108] as have complexes of monophosphinic acid DOTA derivatives conjugated to cyclodextrin scaffolds.[109] A contrast agent based on two Zn^{2+}-dipicolylamine (Zn-dpa) groups conjugated to a Gd(III) chelate reduces the T_1 of labelled compared to unlabelled bacteria, with the possibility of visualizing bacterial infections *in vivo*.[110] Paramagnetic lanthanide complexes enhance sensitivity in ^{19}F NMR.[111] A number of groups have investigated nanosystems for MRI agents.[112,113] Enzyme-responsive contrast agents have been described.[114] Lanthanide complexes of a pyridine-based DTPA-type ligand have favourable MRI and near-infrared-emitting properties, depending on the lanthanide employed.[115] A tetraphosphonated pyridyl ligand affords Gd^{3+} MRI contrast agents that are sensitive to Mg^{2+}.[116] DOTA-tetraamide complexes of Eu^{3+} with *N*-methylquinolinium redox-active functional groups are pH- and redox-sensitive MRI sensors.[117] Conformationally locked Eu^{3+} chelates of substituted DOTA type ligands have been synthesised to eliminate conformational exchange and optimise water exchange.[118] Variable temperature ^{17}O NMR studies have been reported on DTPA complexes, giving evidence for a fluxional process, ascribed to the rotation of the carboxylate groups.[119] Interest continues in utilising optical properties of lanthanide complexes in anion-sensing.[120–122]

Magnetism

A point-charge approach, corrected for covalency, has been used to model the properties of lanthanide single-ion magnets. Values of effective charges and radii have been derived for a variety of halide and nitrogen ligands.[123] There is ever-increasing interest in the magnetic behaviour of lanthanide compounds, especially those of dysprosium(III), on account of its properties, notably the large unquenched orbital moment of Dy^{3+}, and its favourable behaviour in low-symmetry environments, leading to a large number of compounds exhibiting single-molecule magnet (SMM) behaviour. Because these substances can retain spin information over long periods of time at low temperature, there are areas of application in high-density magnetic data storage, quantum computing, spintronics and magnetic refrigeration that are rich in potential. A wide variety of compounds have been investigated, both single-metal and mixed metal (usually 4f–3d) systems; Dy_3 compounds are popular as the desirable slow relaxation behaviour was first noted in a Dy_3 compound. The double decker complex bis(octacyanophthalocyanine)dysprosium(III) is a promising SMM material with potential for making surface arrays by self-assembly.[124] In a comparison of monometallic phthalocyanines with multiple-decker phthalocyaninato dinuclear SMMs, a dual magnetic relaxation process was observed in dinuclear Tb(III)–Pc complexes, in contrast to the mononuclear Tb(III)–Pc complex where there is only a single magnetic relaxation process. In contrast, dinuclear Dy(III)–Pc SMMs exhibited single-component magnetic relaxation behaviour.[125] Addition of peripheral phthalimide derivatives to double-decker phthalocyanine Tb(III) SMMs greatly enhances redox stability without altering the SMM properties.[126] Relaxation behaviour in dysprosium complexes of a tetraaza[14]annulene ligand has

been compared with those of phthalocyanine complexes.[127] $[Dy(hfac)_3(PyNO)]_2$ is a luminescent and sublimable SMM.[128] Use of a bulky N_2 donor in complexes $[Dy(L)(acac)_3]$ (L = dpq, dppz) greatly enhances anisotropic barriers in SMMs.[129] Combining a carbon-rich ruthenium complex with an anisotropic dysprosium ion creates a SMM complex with multiple relaxation processes.[130] Two thermally activated relaxation processes are observed in a mononuclear Dy^{III} complex with a non-Schiff base compartmental ligand.[131] A ligand dimerisation process has been utilised to link two Dy^{III} SMMs into a dinuclear complex that also displays SMM behaviour.[132] Enantiomeric pairs of a dinuclear Dy complex are the first ferroelectric chiral polynuclear lanthanide-based single-molecule magnets.[133] A dinuclear Schiff base complex where the two dysprosium ions are linked by bridging phenolato groups shows single molecule magnetic behaviour.[134] Another Schiff base has been used to create a heterodinuclear $[Zn(L)Dy]^{3+}$ complex which acts as a bifunctional luminescent single-ion magnet.[135] A new type of Dy^{III}-[2 × 2] grid shows slow relaxation of the magnetization.[136] Salen-type ligands have been used to generate triple-decker Dy_3 SMM complexes with slow magnetic relaxation behaviour.[137] A carboxylate-based Dy_2 complex also shows slow magnetic relaxation behaviour,[138] whilst a carbonate-bridged Dy_2 complex with 2,3-quinoxalinediolate ligands is a SMM.[139]

Hydrothermal synthesis affords a family of dinuclear complexes of 3-(1H-tetrazol-5-yl)benzoic acid, $[Ln_2(3\text{-}Htzba)_2(3\text{-}tzba)_2(H_2O)_8] \cdot 4H_2O$ (Ln = Gd, Dy, Eu, Tb, Sm, Er) of which the Dy compound is a SMM.[140] The Dy(III) complex of a Schiff base proligand shows SMM behaviour. The ligand has two further compartments which can be occupied by Mn(II) ions, converting it into a trinuclear mixed 3d–4f complex, a weak ferromagnet at low temperatures, thus switching off the SMM behaviour.[141] Coupling two Dy_3 triangles maximizes the toroidal moment in the resulting Dy_6 complex.[142] Two trinuclear triangular circular helicate dysprosium(III) complexes exhibit SMM behaviour.[143] Whilst several Dy_4 systems have been examined,[144–148] including the first Dy_4 SMM with a toroidal magnetic moment in the ground state;[144] other SMMs involve five,[149,150] six,[151,152] seven,[153] eight[154,155] and twelve[156] dysprosiums.

Abbreviations

$(^{t\text{Bu}}ArOH)_3tacn$	1,4,7-tris(3,5-di-*tert*-butyl-2-hydroxybenzyl)-1,4,7-triazacyclononane
bath	4,7-diphenyl-1,10-phenanthroline
bda	2,2′-bipyridine-6,6′-dicarboxylic acid
binol	(R)-2,2′-dihydroxy-1,1′-binaphthyl
bipy	2,2′-bipyridine
BTB	3,3′-bis(4,4,4-trifluoro-1,3-dioxobutyl)biphenyl
C_2mim	1-ethyl-3-methylimidazolium
C_2C_1mim	1-ethyl-2,3-dimethylimidazolium
C5-BPP	2,6-bis(5-(2,2-dimethylpropyl)-1H-pyrazol-3-yl)pyridine
Cp′	$C_5H_4SiMe_3$
Cp″	$1,3\text{-}C_5H_3(SiMe_3)_2$
Cp‴	$1,2,4\text{-}(Me_3C)_3C_5H_2$
$CyMe_4$-BTBP	6,6′-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydrobenzo-1,2,4-triazin-3-yl)-2,2′-bipyridine

CyMe$_4$-hemi-BTBP	6-(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-1,2,4-benzotriazin-3-yl)-2,2′:6′,2″-terpyridine
dcnm	dicyanonitrosomethanide
dien	diethylenetriamine
diglyme	di(2-methoxyethyl)ether
DIPP	2,6-diisopropylphenyl
DMAP	4-dimethylaminopyridine
dme	1,2-dimethoxyethane
DOTA	1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetate
DPDMG	N,N′-diisopropyl-2-dimethylamidoguanidinato
dppz	dipyrido[3,2-a:20,30-c] phenazine
dpq	dipyrido[3,2-d:20,30-f]quinoxaline
EBI*	ethylenebis(hexamethylindenyl)
D-facam	3-trifluoroacetyl-d-camphor
FOD	6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionate
Hfac	1,1,1,5,5,5-hexafluoro-2,4-pentanedionate
hfbc	3-heptafluorobutyryl camphorate
HOdip	2,6-diisopropylphenol
3-H$_2$tzba	3-(1H-tetrazol-5-yl)benzoic acid
L$^{2\text{-Me}}$	[N(2-MeC$_6$H$_4$)C(Me)]$_2$CH$^-$
L$^{2,6\text{-ipr2}}{}_{\text{Ph}}$	[(2,6-^{i}Pr$_2$C$_6$H$_3$)NC(Me)CHC(Me)N(C$_6$H$_5$)]$^-$
Monoglyme	1,2-dimethoxyethane
naphO	2-naphthoxide
phen	1,10-phenanthroline
piv	pivalate, dimethylpropanoate
PNP$^-$	bis(2-diisopropylphosphino-4-tolyl)amide
^{i}Pr-Pybox	2,6-bis(4R/4S-isopropyl-2-oxazolin-2-yl)pyridine
PyNO	pyridine N-oxide
tepa	tetraethylenepentamine
teta	triethylenetetramine
Tetraglyme	bis[2-(2-methoxyethoxy)ethyl]ether
tren	tris(2-aminoethyl)amine
XPA	(4-X-C$_6$H$_4$NH)P(O)(NC$_4$H$_8$O)$_2$ where X = H, F, Cl and Br

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