Review

Lanthanide phosphine oxide complexes

Andrew W.G. Platt

School of Sciences, Staffordshire University, Leek Road, Stoke on Trent ST4 2DF, UK

ARTICLE INFO

ABSTRACT

Phosphine oxide complexes of lanthanide metal have been studied to elucidate the fundamental aspects of their structural chemistry and to develop important technological applications mainly in the reprocessing of nuclear fuels and in photoluminescent devices but also in other fields such as gas sorption and homogeneous catalysis. The aim of this review is to give an overview of the range of complexes with phosphine oxides and trivalent lanthanide and yttrium ions, their structural features and applications.

© 2016 Elsevier B.V. All rights reserved.

Contents

1. Introduction and scope of the review

Complexes with phosphine oxides are an important area in the coordination chemistry of the lanthanide metals, not only from the fundamental aspects of the chemistry, but also from the wide range of applications which have been explored for these systems.

This review covers developments principally from 2000 onwards although earlier work is mentioned to give context to the later studies and where further studies are limited. Early work on lanthanide complexes was reviewed in 1979 [1]. The studies established that nitrates form a variety of complexes with the composition $[Ln(NO_3)_3(R_3PO)_3]$ (R = Bu, Ph) being particularly favoured. Analysis of infrared spectra led to the conclusion that the metals were 9-coordinate with bidentate nitrates. Triphenylphosphine oxide was extensively studied and variation of reaction conditions allowed the isolation of $[Ln(NO_3)_3(Ph_3PO)_4]$ and $[Ln(NO_3)_2(Ph_3PO)_3]NO_3$. Lanthanide chloride complexes $[LnCl_3(Ph_3PO)_3]$ and $[LnCl_3(Ph_3PO)_4]$ were obtained for all lanthanides whilst the thiocyanate complexes $[Ln(NCS)_3(Ph_3PO)_4]$

were obtained for the lighter metals whilst the smaller lanthanide ions form, presumably, 6-coordinate [Ln(NCS)$_3$(Ph$_3$PO)$_3$]. With the weakly coordinating perchlorate, ionic complexes [Ln(ClO$_4$)$_2$(Ph$_3$PO)$_4$]ClO$_4$ were isolated. The coordination chemistry of lanthanide and actinide halides with neutral oxygen and nitrogen donor ligands was reviewed in 2008, briefly covering phosphine oxide complexes [2]. The content here is ordered according to the number of PO groups in the ligand and then by lanthanide salt. The majority of early studies were on nitrate and halide complexes, but increasingly work on pentane-2,4-dionate complexes is being reported due to the interest in applications of these species to a number of fields. Yttrium has a very similar ionic radius to holmium and its chemistry, like that of the lanthanide metals is mainly that of the +3 oxidation state, and studies of this are also covered in the review. Organometallic complexes are not covered in this review.

2. The nature of the "P=O bond in phosphine oxides

Whilst the phosphorus oxygen bond in R$_3$PO is generally written as P=O its exact nature has been the subject of some debate. An early review summarised the conflicting opinions on the bonding phosphine oxides and concluded that a formal double bond between the phosphorus and oxygen atoms was the best description [3]. Subsequently more theoretical studies have suggested that the PO bond has a strong ionic component and is best represented as R$_3$P$^+$-O$^-$ [4,5]. Experimental support for this formulation comes from ^{17}O solid state NMR studies on two polymorphs of Ph$_3$PO where the chemical shielding tensor and the ^{17}O quadrupolar coupling constant are consistent with its strongly ionic σ-bonded nature [6]. This is of significance to the bonding in lanthanide complexes which is expected to be predominantly electrostatic in nature between the negative O atom and the positively charged lanthanide ion. Also of significance would be the repulsion between the positively charged P and Ln centres which would be expected to make the Ln-O-P angle approach 180° in the absence of geometrical constrains imposed by the ligand, for instance in chelating structures, and secondary interactions in the peripheral structure of the complex.

The basicity of phosphine oxides is also of importance to their coordinating ability. In protic media the basicity is dominated by solvation effects on R$_3$POH$^+$ rather than the inductive effects of the substituents on the phosphorus atom. Thus for MeR$_2$PO the order of basicity with variation in R is Me > Bu > ^{t}Bu [7]. In the gas phase the basicity follows the expected order of the inductive effect of the P-bound groups with the order in R$_3$PO being ^{i}Prop$_3$PO > ^{n}Prop$_3$PO > Et$_3$PO > Me$_3$PO [8]. The gas phase basicity may be more relevant to their metal coordination chemistry as the specific solvation interactions between R$_3$POH$^+$ and protic solvents are likely to be reduced in larger lanthanide complexes where any charge is spread over a larger surface area.

Bond distances within phosphine oxides will affect the steric requirements of the ligands. Structural data showing an increase in the PO distance along the series Me$_2$RPO (R = Me, Et, ^{i}Prop, ^{t}Bu) has been explained on the basis of molecular mechanics calculations as being due to increased steric repulsions and electronegativity effects which also increase the P–C(R) bond length [9].

3. Ligands with 1 PO group

3.1. Complexes with Lanthanide Nitrates

Complexes with trimethylphosphine oxide, Me$_3$PO and triethylphosphine oxide, Et$_3$PO, with Nd(NO$_3$)$_3$ have the composition [Nd(NO$_3$)$_3$(R$_3$PO)$_3$] with the nitrate ions being assigned as ^{2}κ biden-

tate ligands on the basis of infrared spectroscopy [10]. The structure of [Y(NO$_3$)$_3$(Me$_3$PO)$_3$] shows the metal to be 9-coordinate with ^{2}κ nitrates [11]. A useful description for these, and related 9-coordinate geometries, was given which considers the nitrates as pseudo-monodentate ligands [12]. On this basis [Y(NO$_3$)$_3$(Me$_3$PO)$_3$] can be thought of as having a *fac*-octahedral structure. The displacement of nitrate by additional Me$_3$PO is possible giving the ionic [Y(NO$_3$)$_2$(Me$_3$PO)$_4$]NO$_3$. The effect of increasing the size of R$_3$PO has been subject to a systematic study using X-ray crystallography and variable temperature NMR spectroscopy. Triethylphosphine oxide gives [Ln(NO$_3$)$_3$(Et$_3$PO)$_3$] for the lighter lanthanides which have a pseudo *mer*-octahedral geometry, presumably the increasing steric effect of Et$_3$PO compared to Me$_3$PO leading to the change from *fac* to *mer* structures [13]. The complexes of the heavier lanthanides were isolated as mixtures of [Ln(NO$_3$)$_3$(Et$_3$PO)$_3$] and [Ln(NO$_3$)$_3$(Et$_3$PO)$_2$] and the low temperature ^{31}P NMR spectra showed that a number of complexes exist in CD$_2$Cl$_2$ solution. These were assigned on the basis of the results from work with bulkier R$_3$PO (discussed below) as pseudo trigonal bipyramidal [Ln(NO$_3$)$_3$(Et$_3$PO)$_2$] and *fac*- and *mer*-[Ln(NO$_3$)$_3$(Et$_3$PO)$_3$].

For triisopropylphosphine oxide, ^{i}Prop$_3$PO, the pseudo *mer*-octahedral [Ln(NO$_3$)$_3$(^{i}Prop$_3$PO)$_3$] were isolated for Ln = La–Eu [14]. Variable temperature ^{31}P NMR measurements confirm that this geometry was retained in CD$_2$Cl$_2$ solution with a single signal at ambient temperature due to rapid exchange between inequivalent phosphorus environments splitting into 2 resonances with a 2:1 intensity ratio at lower temperatures. For erbium a pseudo *mer*-octahedral ionic complex [Er(NO$_3$)$_2$(^{i}Prop$_3$PO)$_3$(H$_2$O)]NO$_3$ was characterised, whilst for heavier metals a pseudo trigonal bipyramidal complexes [Ln(NO$_3$)$_3$(^{i}Prop$_3$PO)$_2$] (Ln = Yb, Lu) were formed and structurally characterised.

Complexes with triisobutylphosphine oxide, ^{i}Bu$_3$PO, where the bulkier substituents are further removed from the immediate coordination site give pseudo *mer*-octahedral [Ln(NO$_3$)$_3$(^{i}Bu$_3$PO)$_3$] across the entire lanthanide series [15]. The dynamic NMR properties again show the geometry to be retained in solution and that the interconversion of inequivalent phosphine oxides is slower for the heavier lanthanides. Tritertiarybutylphosphine oxide, ^{t}Bu$_3$PO, forms only [Ln(NO$_3$)$_3$(^{t}Bu$_3$PO)$_2$] with 9-coordinate hydrates Ln = La–Nd and pseudo–trigonal bipyramidal complexes for the heavier lanthanides [16]. In the solid state the trigonal bipyramidal compounds exists as two isomers; one with an equatorial belt comprising either three essentially coplanar nitrates and linear PO-Ln-OP and the other with one of the nitrates twisted out of the equatorial plane and a non-linear PO-Ln-OP arrangement. The structures adopted in the Lu complex are shown in Fig. 1.

Tricyclohexylphosphine oxide, Cy$_3$PO, which has a similar bulk to ^{t}Bu$_3$PO based on the cone angles of the respective phosphines [17] gives [Ln(NO$_3$)$_3$(Cy$_3$PO)$_3$]·xEtOH the structures of which show subtle effects due to the lanthanide contraction [18]. All the complexes have the pseudo *mer*-octahedral arrangement with the lattice ethanol (where present) hydrogen bonded to an oxygen of the coordinated nitrate. With the heavier metals there is an increased tendency to relieve steric strain caused by the lanthanide contraction by forming monodentate nitrates. Thus the structure of [Er(NO$_3$)$_3$(Cy$_3$PO)$_3$] has two molecules in the unit cell, one with three ^{2}η nitrates and one with two ^{2}η one ^{1}η nitrate, whilst the Tm and Yb complexes have two ^{2}η and one ^{1}η nitrate as shown in Fig. 2.

Complexes of tributylphosphine oxide, ^{n}Bu$_3$PO, and trioctylphosphine oxide, Oct$_3$PO, have the composition [Ln(NO$_3$)$_3$(R$_3$PO)$_3$] [19]. Analysis of the infrared spectra led to the conclusion that ionic nitrate was present. A study of the complex formation of Nd(NO$_3$)$_3$ with various organophosphorus reagents in supercritical CO$_2$ concluded on the basis of electronic spectroscopy that [Nd(NO$_3$)$_3$(^{n}Bu$_3$PO)$_5$] was formed, but no materials were isolated and further characterisation was not given [20]. Trioctylphosphine

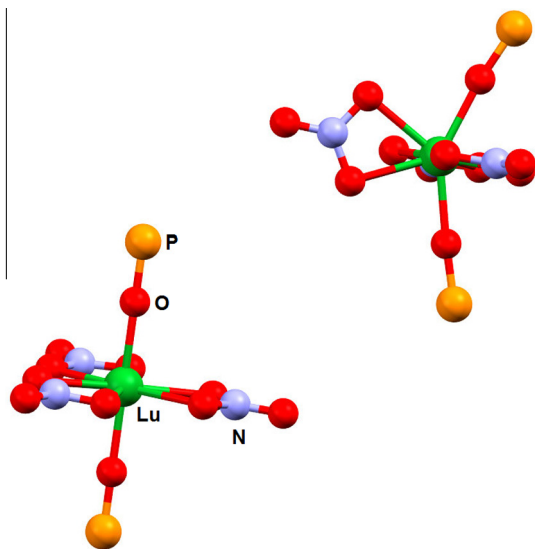**Fig. 1.** The core structure of [Lu(NO₃)₃(ᵗBu₃PO)₂] (hydrogen and carbon atoms omitted for clarity) Reproduced using coordinates from Ref. [16].
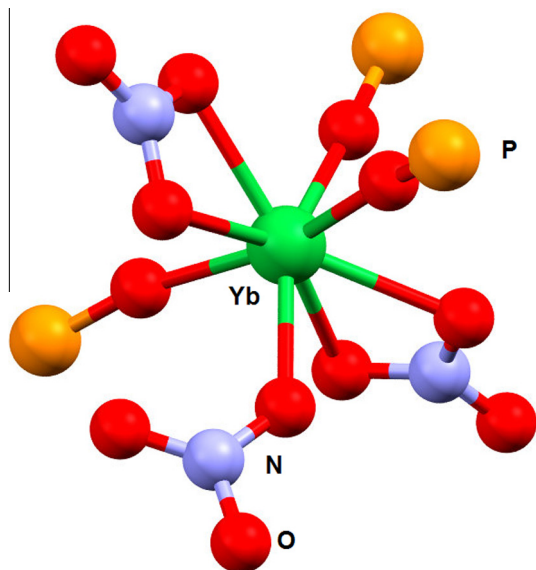
Fig. 2. The core structure of [Yb(NO₃)₃(Cy₃PO)₃] (hydrogen and carbon atoms omitted for clarity) Reproduced using coordinates from Ref. [18].

oxide has been used as an extractant for Nd^{3+} in the presence of dinonylphenylphosphoric acid in nitric acid[21]. Extraction selectivity of Sc^{3+} over Y^{3+} and Ln^{3+} was demonstrated by mixed alkylphosphine oxides using alkylammonium based ionic liquids in nitric acid media and whilst the nature of the extracted complexes was not explored, they could reasonably be assumed to contain nitrate [22]. The thermodynamics of the extraction of lanthanide ions from aqueous solution by Oct_3PO has been determined and the $\Delta H_{extr} \sim 29$ kJmol^{-1} found for most of the lanthanides [23]. The metals are extracted as [Ln(NO₃)₃(Oct₃PO)₃].

Triphenylphosphine oxide complexes have been studied in depth and show variations in structures depending on the ionic radius of the metal and the reaction conditions employed in their synthesis [24]. The 9-coordinate complexes [Ln(NO₃)₃(Ph₃PO)₃] are formed for all Ln. In the presence of a large excess of Ph₃PO, [Ln(NO₃)₃(Ph₃PO)₄] are formed and their structures fall into two types. Nine coordinate structures with two $^2\eta$ and one $^1\eta$ nitrate

are formed for the lighter La–Nd as acetone solvates whilst for the heavier lanthanides (Tb–Lu) steric congestion is reduced by the formation of 8-coordinate ionic species [Ln(NO₃)₂(Ph₃PO)₄] NO₃. Mixed ligand complexes [Ln(NO₃)₃(Phen)(Ph₃PO)₂] and [Ln(NO₃)₃(EtOH)(Ph₃PO)₂] have been structurally characterised [25]. The electronic spectra show that [Ln(NO₃)₃(Phen)(Ph₃PO)₂] have promise as photoluminescent materials. The terbium complex [Tb(PhCOCO₂)₂(NO₃)(Ph₃PO)₂] has been prepared and its fluorescence spectra show that Ph₃PO gives a relatively lower emission intensity compared to similar complexes which contain bipyridyl and phenanthroline ligands [26]. The structure of a mixed nitrate-thiocyanate complex [Eu(NO₃)(NCS)₂(Ph₃PO)₃] has also been reported [27]. A rare example of a cerium(IV) complex [Ce(NO₃)₄(Ph₃PO)₂] has been structurally characterised and shows similarities to the structures of the Ln(III) complexes with bulky R₃PO in that it has an equatorial arrangement of nitrates with the phosphine oxides occupying "axial" positions [28]. Attempts to prepare lanthanide complexes with the bulkier trimesitylphosphine oxide were not successful [29]. Diphenylmethylphosphine oxide, Ph₂MePO, forms pseudo *fac*-octahedral complexes [12]. The 9-coordinate [Ln(NO₃)₃(Ph₂MePO)₃] (Ln = Pr–Tb) are stable in solution whilst, when Ln = Ho–Lu, partial ionisation occurs to give [Ln(NO₃)₂(Ph₂MePO)₄]$^+$ which were isolated and structurally characterised as the PF₆$^-$ salts. The larger La can accommodate further Ph₂MePO giving the 10-coordinate [Ln(NO₃)₃(Ph₂MePO)₄] as an acetone solvate. A similar pseudo *fac*-octahedral complex, [Tb(NO₃)₃(Ph₂P(O)C₂H₄PPh₂)₃], is formed by mixed phosphine oxide–phosphine ligand Ph₂P(O)C₂H₄PPh₂ [30]. The solution ^{31}P NMR spectra show that the primary interaction with the metal is with the phosphoryl oxygen as expected, although the relatively small paramagnetic shifts for the Ce and Tb complexes indicate that significant ligand dissociation occurs in the alcohol solvents used for the measurements.

Because of their application to nuclear fuels reprocessing carbamoylphosphine oxides, (CMPOs), Fig. 3, have been studied both experimentally and theoretically with an emphasis on their use as extractants.

An NMR study of the interaction of CMPO (R₁ = Ph, R₂ = Oct, R₃ = R₄ = ^{i}Bu) with lanthanide nitrates found that CMPO binds in a bidentate manner to Ce, Sm and Eu in metal: ligand ratios 1:3 [31]. Later studies of the same ligand found that the extraction of lanthanide nitrate complexes gave between 40% and 50% transport of the lanthanide into a hydrocarbon phase [32]. Theoretical studies of CMPO (R₁ = R₂ = R₃ = R₄ = Me) indicate that bidentate bonding is favoured and that the bonding becomes stronger along the lanthanide series La to Yb [33]. A later density function study concluded that the gas phase binding energies of species such as [Eu(CMPO)(H₂O)₅]$^{3+}$, [Eu(CMPO)(NO₃)(H₂O)₃]$^{2+}$ and [Eu(CMPO)(NO₃)₂(H₂O)]$^+$ (R₁ = Ph, R₂ = Oct, R₃ = R₄ = ^{i}Bu) range between −462.5 to −1027.6 kJmol^{-1} and that in the optimised structures CMPO is bidentate in all cases [34]. Electrochemical oxidation of [Ce(NO₃)₃(CMPO)₃] (R₁ = Ph, R₂ = Oct, R₃ = R₄ = ^{i}Bu) produced a Ce(IV) complex, but this was not isolated or further characterised [35]. The unstable Ce(IV) complex [Ce(NO₃)₃(Ph₂P(O)CHCOPh)(Ph₂P(O)CH₂COPh)] was isolated from the reaction between (NH₄)₂Ce(NO₃)₆ and Ph₂P(O)CH₂COPh and characterised by elemental analysis and infrared spectroscopy [36].

The coordination chemistry of a series of pyridine N-oxide functionalised CMPOs has been studied. The structures of the ligands are shown in Fig. 3.

Theoretical calculations on the coordinating ability of (**1**)–(**3**) with lanthanide nitrates indicate that they should be able to adopt tri-, tetra- and pentadentate modes of bonding with minimal strain. The crystal structures of complexes with Ln(NO₃)₃ show that a chelating–bridging pattern of bonding is adopted in all cases [37]. Chelating PO–NO bonding is adopted by (2-CF₃C₆H₄)₂P(O)
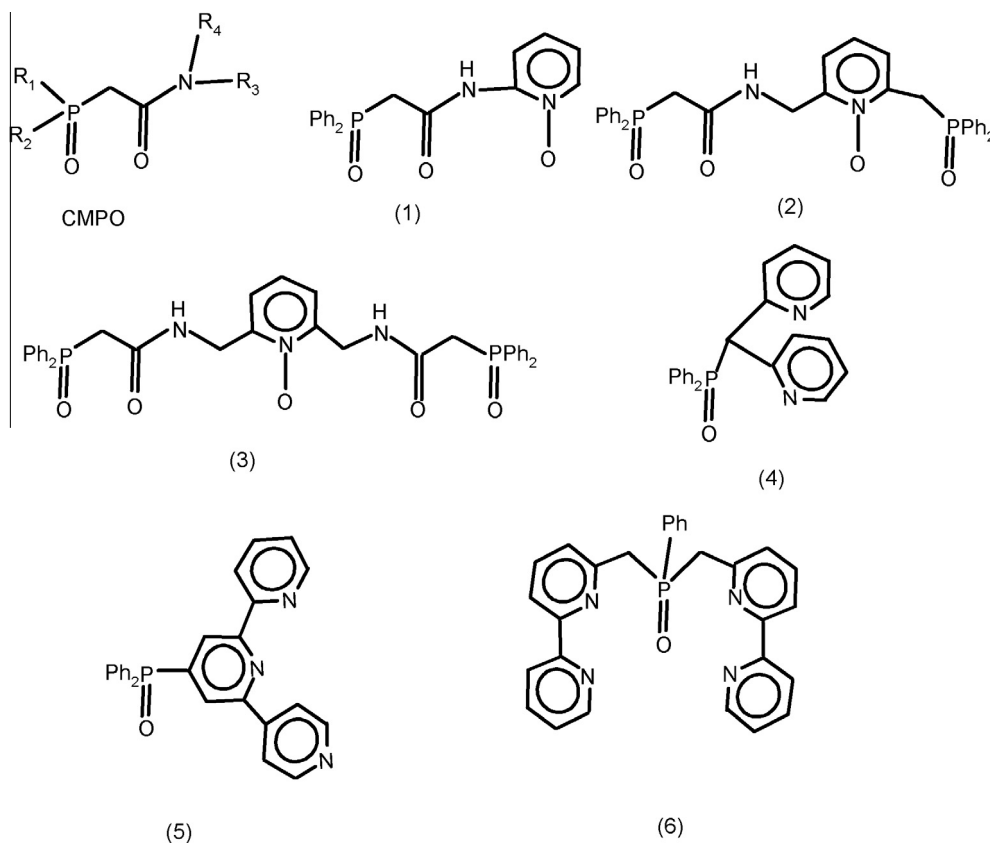
Fig. 3. The structures of compounds (**1**)–(**6**).

$CH_2C_5H_5NO$ in its complex with $Yb(NO_3)_3$ [38]. Pyridine function-alised phosphine oxides tend to bond by the phosphoryl oxygen only. Thus the structure of $[Er(NO_3)_3(4)(MeOH)_2]$ is 9-coordinate with (**4**) acting as a monodentate ligand [39]. Analysis of the electronic spectra in the $Eu(NO_3)_3$–(**5**) system indicated that three distinct complexes are formed namely $[Eu(NO_3)_3(5)]$, $[Eu_2(NO_3)_6(5)]$ and $[Eu(NO_3)_3(5)_2]$ [40]. $[Eu(NO_3)_3(5)]·3H_2O$ shows energy transfer from the terpy to the metal centre. The coordination of the terpy units is strongly solvent dependent. In CH_3CN they are coordinated whilst in oxygen donor solvents such as DMSO and DMF the terpy is displaced by the solvent. The *bis*-bipyridylphosphine oxide (**6**) forms 1:1 complexes $Ln(NO_3)_3(6)·xH_2O$ Ln = Eu, Gd, Tb [41]. The crystal structures of the Tb complexes $[Tb(NO_3)_3(6)(H_2O)(MeOH)]$ and $[Tb(NO_3)_3(6)(MeOH)_2]$ show that the metal is 9-coordinate in each case and that (**6**) bonds via the PO only. The nitrate complexes show an enhanced luminescence intensity compared to the triflate or halide complexes which has suggested potential application for anion detection.

The lanthanide coordination chemistry of a series of 4,5-dihydrooxazole (**7**), Fig. 4, and benzoxazole, (**8**), functionalised phosphine oxides has led to the structural characterisation of several lanthanide nitrate complexes [42]. The ligands can bond in a monodentate fashion as in $[Nd(NO_3)_3(7)_2(MeOH)]$, as a chelate in $[Nd(NO_3)_3(7)_2]$ and $[Nd(NO_3)_3(8)_2]·3CHCl_3$ or can H-bond to coordinated water via the N-atom in $[Yb(NO_3)_3(8)(H_2O)]$.

3.2. Complexes with lanthanide halides

Probably as a result of the high lattice energies of lanthanide fluorides, there are no reports of phosphine oxide complexes with LnF_3 and attempts to prepare CeF_4 complexes using $[CeF_4(DMSO)_2]$ as a precursor were unsuccessful [43]. The structure of $[Ce(Me_3PO)_4(H_2O)_4]Cl_3·3H_2O$ has an 8-coordinate cerium with

the chloride ions not bonded to the metal [44]. Reactions of hydrated $LnCl_3$ with an excess of Me_3PO led to the isolation of $[Ln(Me_3PO)_4Cl_3·xH_2O]$ for which crystals suitable for X-ray diffraction studies could not be obtained [45]. The La and Ce complexes are non-conducting in nitromethane and are presumably 7-coordinate. In the presence of NH_4PF_6 the series of homoleptic complexes $[Ln(Me_3PO)_6][PF_6]_3$ were isolated and structurally characterised for Ln = Pr, Gd and Dy. The complexes have a slightly distorted octahedral arrangement of Me_3PO around the lanthanide ion. Yttrium forms a similar 6-coordinate cation on reaction of YBr_3 with Me_3PO [46]. Hydrated lanthanide chlorides react with Cy_3PO to give $[Ln(H_2O)_5(Cy_3PO)_2]·Cy_3PO·Cl_3$ which were structurally characterised for Ln = Dy, Er [47]. The metals are 7-coordinate with a pentagonal bipyramidal arrangement comprising five H_2O in the equatorial plane and Cy_3PO occupying axial positions. The remaining Cy_3PO and the chloride ions are hydrogen bonded to the coordinated water molecules. Solution ^{31}P NMR spectroscopy shows that the complexes are labile with rapid exchange between lanthanide and H-bonded Cy_3PO at ambient temperature for the La complex. This exchange is slow for the heavier lanthanides. The presence of local D_{5h} symmetry has been exploited in suppressing rapid quantum tunnelling of magnetisation in the Dy complex [48].

Complexes between $LnCl_3$ and Ph_3PO have been extensively studied. Compounds with varying composition can be obtained by appropriate changes to reaction conditions [49]. The series of complexes $[LnCl_3(Ph_3PO)_3]$ and $[LnCl_2(Ph_3PO)_4]Cl$ from which $[LnCl_2(Ph_3PO)_4][PF_6]$ can be obtained and have been characterised. The structures are based on *mer*- and *trans*-octahedra for the *tris* and *tetrakis* complexes respectively. In non-coordinating solvents ^{31}P NMR spectroscopy shows that $[LnCl_3(Ph_3PO)_3]$ and $[LnCl_2(Ph_3PO)_4]^+$ interconvert to some extent with the *tris* complexes being favoured for the lighter lanthanides whilst the heavier lanthanides prefer the ionic complexes. Yttrium chloride forms
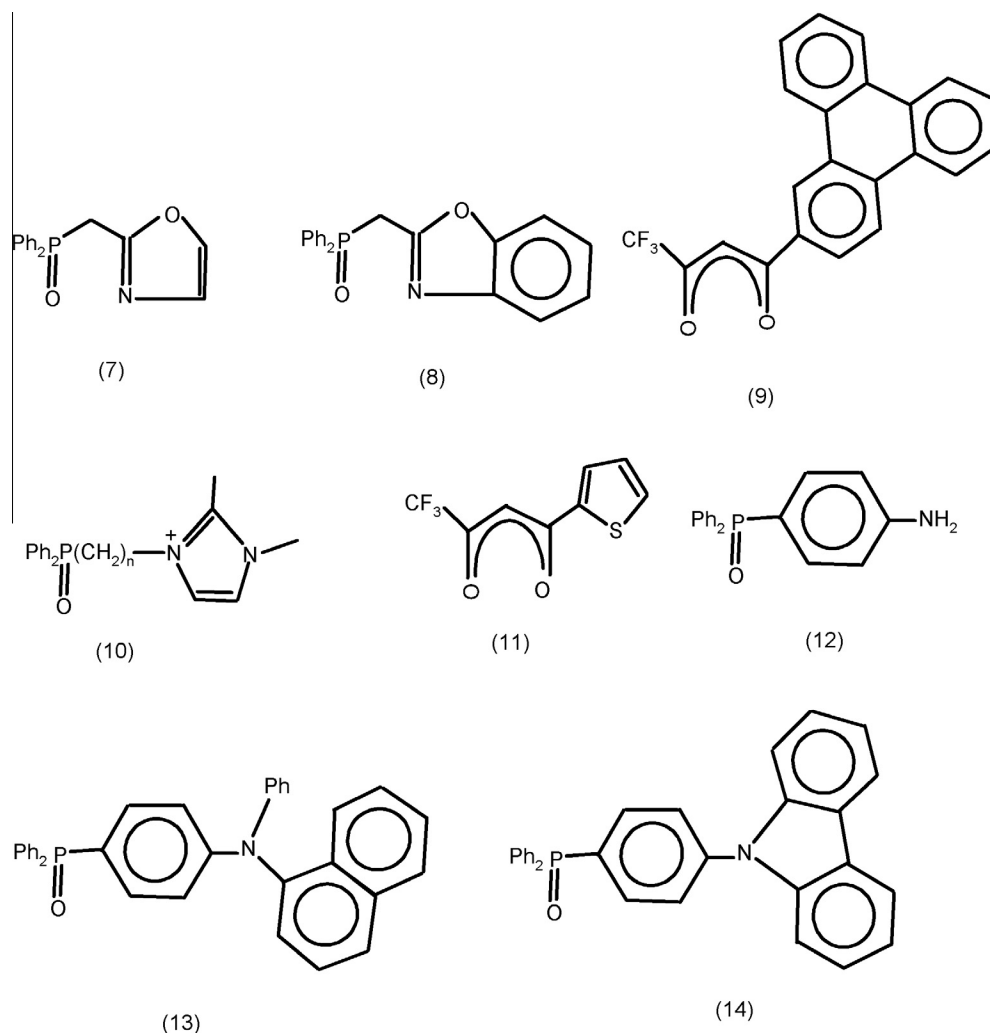
Fig. 4. The structures of compounds (**7**)–(**14**).

similar *trans*-octahedral [YCl$_2$(Ph$_3$PO)$_4$]Cl [46]. With anhydrous LaCl$_3$ in the presence of FeCl$_3$ as a chloride ion acceptor the octahedral complex [LaCl(Ph$_3$PO)$_5$][FeCl$_4$]$_2$ was formed [50]. The ^{31}P NMR spectra of the analogous yttrium complex showed that the complex is stereochemically rigid on the NMR timescale.

Hydrated lanthanide bromides form two types of complex with Cy$_3$PO [51]. The *mer*-octahedral [LnBr$_3$(Cy$_3$PO)$_3$], Ln = La, Pr, Nd, Gd and Ho, and pentagonal bipyramidal [Ln(H$_2$O)$_5$(Cy$_3$PO)$_2$]·(Cy$_3$PO)$_2$Br$_3$, Ln = Dy, Er and Yb were structurally characterised. As with the chloro complexes, the structures of the pentagonal bipyramidal complexes consist of a [Ln(H$_2$O)$_5$(Cy$_3$PO)$_2$]$^{3+}$ core with the remaining Cy$_3$PO and bromide ions hydrogen bonded to the coordinated water molecules. Reactions with lower metal: Cy$_3$PO ratios led to the isolation of [Lu(H$_2$O)$_5$(Cy$_3$PO)$_2$]·Cy$_3$PO·Br$_3$ and [Lu(H$_2$O)$_5$(Cy$_3$PO)$_2$]·Br$_3$·(EtOH)$_2$, the latter being fully structurally characterised. Yttrium bromide gives the *trans*-octahedral [YBr$_2$(Ph$_3$PO)$_4$][PF$_6$] [46] and lanthanide bromides give analogous complexes which were structurally characterised for Ln = Nd, Gd and Yb [52]. The iodo complexes [LnI$_2$(Ph$_3$PO)$_4$]I have been prepared and structures also show the *trans*-octahedral geometry (Ln = La, Ce, Nd) [53]. Quantum mechanical studies on [LnCl$_3$(Me$_2$P(O)CH$_2$CONMe$_2$)] show, as for the corresponding nitrates, that the CMPO ligand marginally favours the chelating mode of bonding compared to monodentate PO coordination [33].

3.3. Complexes with lanthanide β-diketonates

The complex [Dy(Acac)$_3$(Ph$_3$PO)$_2$] has been characterised and synthesised *in situ* to produce a doped xerogel where the presence of Ph$_3$PO increases the emission intensity compared to complexes with 1,10-phenanthroline [54]. Fluorinated pentane 2,4-dionates have been studied with the emphasis on their potential application in optical devices based on the luminescent properties of the lanthanide ions. The anionic and neutral groups bonded to the lanthanide ions are excited to the S$_1$ state with energy transfer to the T$_1$ state followed by transfer to an excited state of Ln^{3+} followed by emission characteristic of the lanthanide ion. Both the nature of the anion and neutral ligand have a strong influence on the emission characteristics of the complexes. Modification of both the pentane-2,4-dionate and phosphine oxide groups can be made relatively easily to optimise the photophysical properties of the complexes. The complexes [Er(CF$_3$COCXCOCF$_3$)$_3$((C$_6$F$_5$)$_3$PO)$_2$] (X = H, F) are 8-coordinate with a square antiprismatic geometry [55]. The presence of (C$_6$F$_5$)$_3$PO increases the near infrared emission intensity of Er^{3+} with the X = F complex having the longest decay time. Similar structures were reported for [Eu(CF$_3$COCFCOCF$_3$)$_3$((C$_6$F$_5$)$_3$PO)$_2$] and [Er(CF$_3$COCFCOCF$_3$)$_3$(Ph$_3$PO)$_2$] [56] and the solution properties were studied by variable temperature ^{19}F and ^{31}P NMR spectroscopy. These indicated that reversible dissociation of the

phosphine oxide occurs at room temperature and is slow at 173 K. The structures of several [Eu(CF$_3$COCHCOCF$_3$)$_3$(phosphine oxide)$_2$] complexes (phosphine oxide = Ph$_3$PO, (4-MeC$_6$H$_4$)Ph$_2$PO, (4-MeC$_6$H$_4$)$_3$PO, and (2-PhOC$_6$H$_4$)Ph$_2$PO) have been reported and are square antiprismatic or trigonal dodecahedral [57]. Emission quantum yields of 72% in acetone-d$_6$ and 85% in the solid state are reported for [Eu(CF$_3$COCHCOCF$_3$)$_3$(2-PhOC$_6$H$_4$)Ph$_2$PO)$_2$]. Tri-octylphosphine oxide complexes of the triphenylene functionalised pentane-2,4-dionate, (9), have been prepared and the structure of [Eu(NO$_3$)(9)$_2$(Oct$_3$PO)$_2$] determined [58]. The luminescent quantum yields of [Eu(9)$_3$(H$_2$O)(EtOH)] and [Eu(9)$_3$(H$_2$O)(Oct$_3$PO)] are increased by replacing H$_2$O and EtOH with Oct$_3$PO.

The phosphine oxide functionalised ionic liquids, (10), have been evaluated as tunable complexation agents by altering the chain length, n [59]. Increasing n increases the binding ability of (10) to lanthanide ions. The structure of the zwitterionic [Eu(CF$_3$COCHCOCF$_3$)$_4$(10)] (n = 3) has been determined and is a distorted tricapped trigonal prism. Diphenylphosphine oxide substituted ruthenocene, CpRuC$_5$H$_4$POPh$_2$, forms an 8-coordinate [Eu(CF$_3$COCHCOCF$_3$)$_3$(CpRuC$_5$H$_4$POPh$_2$)$_2$] which shows a considerable enhancement of its luminescence under potentiostatic polarisation in acetonitrile solution [60]. This was rationalised as being due to repulsion of the positively charged ruthenocenyl cations formed leading to a change in geometry and offers potential in switchable photoluminescent devices. Intramolecular energy transfer from ligands to lanthanide ions in thenoyltrifluoroacetonate, (11), complexes has been investigated and increased luminescent intensity has been observed for [Sm(11)$_3$(Ph$_3$PO)$_2$] compared to [Sm(11)$_3$(H$_2$O)$_2$] due to the removal of efficient fluorescent quenching by the OH vibrations [61]. The europium complexes [Eu(11)$_2$(NO$_3$)(Ph$_3$PO)$_2$] and [Eu(11)$_3$(Ph$_3$PO)$_2$] also show promising photoluminescent and tribioluminescent properties [62]. Amino-functionalised phosphine oxides (12–14) were incorporated as hole-transport groups in [Eu(11)$_3$(12)$_2$], [Eu(11)$_3$(13)$_2$] and [Eu(11)$_3$(14)$_2$] [63]. The energy of the S$_1$ excited state for (12)–(14) is similar to that of (11) which leads to efficient energy transfer

from the neutral phosphine oxide ligand to the ^{5}D$_0$ state of europium. Further work on [Eu(11)$_3$(12)$_2$] established that the energy transfer sequence from the S$_1$ level of (12) is S$_1^{(12)} \rightarrow$ S$_1^{(11)} \rightarrow$ T$_1^{(12)} \rightarrow$ T$_1^{(11)} \rightarrow$ ^{5}D$_0^{Eu}$ [64]. The terbium complex [Tb(11)$_2$(NO$_3$)(Ph$_3$PO)$_2$] has a distorted dodecahedral structure and its photoluminescence indicates it has potential application as a green source in organic light emitting devices [65].

The europium complex of 3-phenyl-4-benzoyl-5-isoxazonate, (15), (Ln = Eu), Fig. 5, forms [(15)(Ph$_3$PO)$_2$] and [(15)(Oct$_3$PO)$_2$] [66]. Theoretical calculations indicate that the complexes should be an approximate tricapped trigonal prism for the Ph$_3$PO structure whilst with Oct$_3$PO a square antiprismatic structure is predicted. The Oct$_3$PO complex shows more efficient ligand to metal energy transfer that the Ph$_3$PO analogue. Triphenylphosphine oxide complexes of lanthanide 1-phenyl-3-methyl-4-isobutyryl-5-pyrazolo-nates (16), [(16)(Ph$_3$PO)$_2$](Ln = Nd [67], and Sm [68]), and of erbium 1-phenyl-3-methyl-4-tert-butylbenzoyl-5-pyrazonolonate (17), [(17)(Ph$_3$PO)] [69] all show intense near infrared emission under U.V. irradiation. The structure of the erbium complex has been determined and is a distorted monocapped trigonal prism.

3.4. Complexes with miscellaneous lanthanide salts

The structure of [Nd(NCS)$_3$(Ph$_3$PO)$_4$] is a slightly distorted capped trigonal prism [70] and [Tb(NCS)$_3$(Ph$_3$PO)$_3$] has a fac-octahedral geometry [71]. In both cases the thiocyanate is N-bonded as expected.

The structures of [Ln(OTf)$_2$(Ph$_3$PO)$_4$](OTf) for Ln = Ce [53] and Nd and Lu [72] show that two triflates remain bonded to the metal. The Ce and Nd complexes contain one bidentate and one monodentate triflate whilst as a result of the smaller ionic radius in the Lu complex both triflates are monodentate. The complex Eu(OTf)$_3$(5)$_2$·3H$_2$O has been prepared but the structure was not determined [40]. The structures of the triphenylphosphine oxide complexes of neodymium dithionate, [Nd$_2$(S$_2$O$_6$)$_3$(Ph$_3$PO)$_4$(H$_2$O)$_8$] [73] and praseodymium dithionate, [Pr$_2$(S$_2$O$_6$)$_3$(Ph$_3$PO)$_6$(H$_2$O)$_6$]
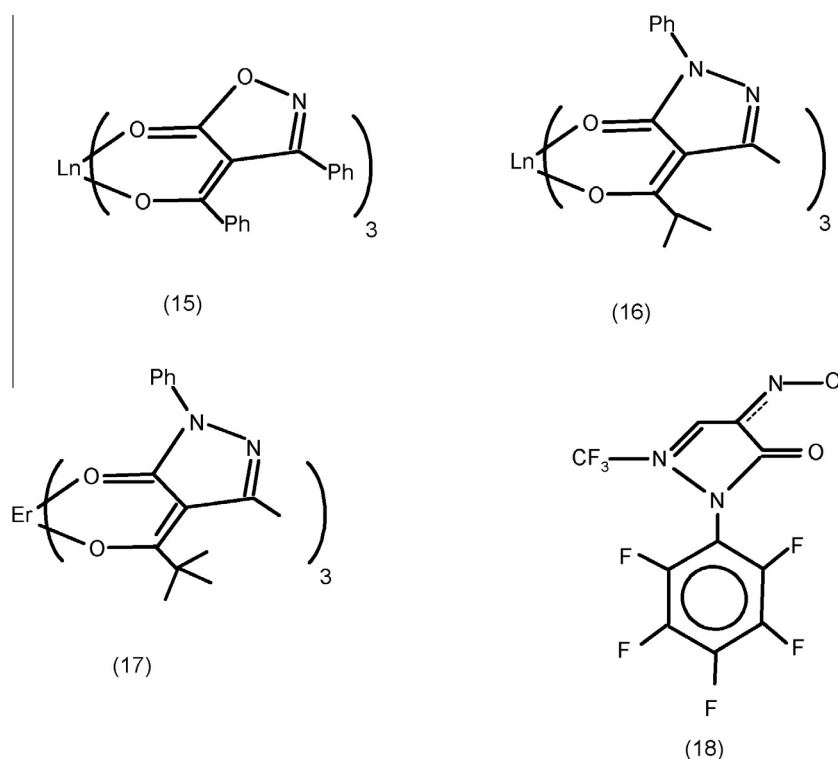

(15)

(16)

(17)

(18)

Fig. 5. The structures of compounds (15)–(18).

[74] have been reported. The neodymium complex has a 9-coordinate metal in which two dithionate ions bind as monodentate ligands with the third bridging between two metals forming a H-bonded dimer. In the praseodymium complex the metal is 8-coordinate as a result of the presence of a further bulky Ph_3PO ligand. The structures of La and Pr triflate complexes of $Ph(C_5H_5NOCH_2)_2PO$ were determined as $[La(Ph(C_5H_5NOCH_2)_2PO)(OTf)_2(MeOH)_3(H_2O)](OTf)$ and $[Pr(Ph(C_5H_5NOCH_2)_2PO)(OTf)(MeOH)_4](OTf)_2$ with $Ph(C_5H_5NOCH_2)_2PO$ acting as a tridentate ligand and the triflate bound via a single oxygen atom in both cases [39].

In the presence of aqueous ammonia a two dimensional network $[Pr_2(NO_3)_3(Ph_2P(O)(CH_2)_4COO)_3]$ is formed on reaction of $Pr(NO_3)_3$ with $Ph_2P(O)(CH_2)_4COOH$ in methanol, whilst under the same conditions a three dimensional framework is produced by the reaction in water [75]. The single crystal X-ray structures show that the carboxylate groups acts in a bridging-chelating manner. The reaction of $(4-HO_2C-C_6H_4)_3PO$ with lanthanide nitrates under solvothermal conditions in $DMF/H_2O/MeOH$ with a small quantity of nitric acid led to the isolation of 3-dimensional networks of $[Ln(4-O_2C-C_6H_4)_3PO]$, Ln = Nd, Sm, Gd [76]. The higher gas sorption properties of the Gd complex were accounted for by the interaction between the field gradient produced by Ln^{3+} and the quadrupole moment of the gas molecules, H_2 and CO_2 in this case. Similar gas sorption properties were also reported for the terbium complex $[Tb(4-O_2C-C_6H_4)_3PO(H_2O)]\cdot DMF\cdot(H_2O)_2$ which has an 8-coordinate structure [77]. The structure has a 2-dimensional pore network and the DMF and two water molecules are located in the void spaces. The hydrogen uptake was particularly high (1.96%wt) for this compound and similarly high values for the uptake of CO_2 and O_2 were measured. Excitation of the phosphine oxide at 330 nm led to Tb based emission and this displayed a reversible two fold increase in luminosity on desolvation under vacuum. The structures of $[Me_2NH_2][Ln_2((4-O_2C-C_6H_4)_3PO)_2(O_2CH)](DMF)_n(H_2O)_m$ Ln = Dy n = 3, m = 3 [78] prepared under solvothermal conditions and Ln = Y, Sm- Lu n = 4, m = 6 [79] by microwave assisted solvothermal synthesis, have also been determined. The complexes have good gas sorption properties as a result of their open framework structures.

Tris-chelate phosphine oxide- alkoxide complexes $[Ln({}^tBu_2P(O)CH_2CHO{}^tBu)_3]$ with Ln = Y, Eu, Er and Yb have been synthesised by reaction of the alcohol with $Ln(N(SiMe_3)_2)_3$ at $-80\,°C$ [80]. The smaller lanthanides required longer for the reaction to proceed to completion. The complexes are formed in a mixture in which 80% comprises the (RRR) and (SSS) enantiomers whilst the remaining 20% consists of the (RRS) and (SSR) forms. The structures of $[Ln({}^tBu_2P(O)CH_2CHO{}^tBu)_2N(SiMe_3)_2]$ Ln = Y and Er were also reported. The *tris*-chelate complexes were found to be active catalysts for the stereoselective polymerisation of *rac*-lactide giving highly isotactic polylactic acid [81].

The $(C_6F_5)_3PO$ complexes with the erbium salt of the nitrosopyrazolone (18), $[Er(18)_3((C_6F_5)_3PO)_n]$ (n = 1,3) showed near infrared emission with long luminescent lifetimes [82].

4. Ligands with 2 P=O groups

In this section methylene spacer groups $(CH_2)_n$ are discussed first followed by spacer based mainly on aromatic rings.

4.1. Complexes with lanthanide nitrates

Complexes with $Ph_2P(O)CH_2P(O)Ph_2$, (19), have been characterised and exhibit a variety of structures [83]. With low ratios of metal to ligand in acetonitrile ionic complexes $[Ln(NO_3)_2(19)_2][Ln(NO_3)_4(19)]$ Ln = Pr, Eu were formed in which the cation has an 8-coordinate metal and the metal in the anion is 10-coordinate. $[Ln(NO_3)_2(19)_2(H_2O)]NO_3$ are formed in ethanol Ln = Nd, Gd, Ho with the ionic nitrate hydrogen bonded to the coordinated water. Heating the complexes in the solid state leads to ligand redistribution reactions which give yellow $[Ln(NO_3)(19)_3](NO_3)_2$ which were structurally characterised for Ln = Gd, Yb. The structures $Ln(NO_3)_3$ complexes of $(Ph_2P(O))_2CHCH_2COMe$, (20), have been determined and show $[Ln(NO_3)_3(20)_2]$ (Ln = La, Nd) to be isostructural with bidentate nitrates and (20) bonding through the phosphoryl oxygen atoms only [84]. Ionic complexes analogous to those formed by (19) were crystallised from ethanol as $[Nd(NO_3)_2(20)_2]NO_3\cdot EtOH$. Solution multinuclear NMR spectroscopy shows that a variety of coordination modes for (20) occur in solution such as tridentate which depend on the size of the cation. Thus in acetonitrile solution in the cation $[Nd(NO_3)_2(20)_2]^+$, (20) acts as both a tridentate and bidentate ligand, whilst in $[Lu(NO_3)_2(20)_2]^+$ it is present as both a bidentate and monodentate ligand.

The reaction between $Ph_2P(O)(CH_2)_2P(O)Ph_2$, (21), and $Pr(NO_3)_3$ under solvothermal conditions gave polymeric $[Pr_2(NO_3)_6(21)_3]$ which has a two-dimensional coordination network in which the metal ion is 9-coordinate [85]. The cerium(IV) complex $[Ce(NO_3)_4({}^tBuPhP(O)C_2H_4P(O)Ph{}^tBu)_2$ was isolated from the reaction of the ligand with $(NH_4)_2Ce(NO_3)_6$ [86]. Infrared spectroscopy suggests a similar structure to the Ph_3PO complex which implies it is polymeric. The 1,3-diphenylphosphinopropane derivative (22), Fig. 6, gives $[Pr(NO_3)_3(22)]$ in which (22) acts as a bidentate ligand bonding through one PO and one NO, with the other PO group bonded to a second Pr centre giving a polymeric chain [87].

The mixed phosphine–phosphine oxides $CH(CH_2PAr_2)(CH_2P(O)Ar_2)_2$ (Ar = Ph, $4-MeC_6H_4$, $2-MeC_6H_4$, $2,5-Me_2C_6H_3$) form 1:1 complexes with $Y(NO_3)_3$. Solution ${}^{31}P$ NMR spectroscopy shows is coordinated by the two PO groups with ${}^2J_{YP}$ coupling clearly resolved whilst the phosphine group, as expected, does not interact with the metal[88]. The crystal structure of $[Y(NO_3)_3(CH(CH_2PPh_2)(CH_2P(O)Ph_2)_2)(Ph_3PO)]$ shows the complex to have a distorted tricapped trigonal-prismatic geometry.

Binuclear complexes are formed between lanthanide nitrates and 1,4-*bis*-(diphenylphosphino)butane dioxide (23) under solvothermal conditions[89]. The phosphine oxide acts as a bridging and chelating ligand giving $[Ln(NO_3)_3(23)-\mu-(23)-Ln(NO_3)_3(23)]$ Ln = Pr, Nd, Sm, Dy, Lu with a pseudo-octahedral geometry about the metal as is common for complexes with monodentate phosphine oxides. Increasing the chain length caused further changes in the structure with complexes of 1,6-*bis*-(diphenylphosphino)hexane dioxide (24), having a polymeric ionic composition $[Ln(NO_3)_3(24)_2]_n(NO_3)_n$ Ln = Pr, Sm, Dy, Lu [90]. The geometry about the metal ion is again pseudo-octahedral with the phosphine oxides bridging between two lanthanide centres giving a two-dimensional network.

Complexes with lanthanide nitrates and the phosphine oxide substituted ferrocene, (25), can form a variety of complexes[91]. It acts in both chelating and bridging modes in $[La(NO_3)_3(25)-\mu(25)-La(NO_3)_3(25)]$ whilst europium and holmium nitrates give ionic complexes $[Ln(NO_3)_2(25)_2]_2[Ln(NO_3)_5]$ and lutetium nitrate gives $[Ln(NO_3)_2(25)_2]NO_3$. Erbium nitrate forms a similar cationic complex in which the geometry around the metal is pseudo-octahedral [92].

With a rigid spacer unit between the two PO groups the capacity of ligands to chelate to a single metal is much reduced and (26) forms coordination polymers $[Pr_2(NO_3)_6(26)_3]_n$ in which the metal is 9-coordinate [92]. Microanalytical data and infrared spectroscopy indicate that the complexes of the later lanthanides have a 2:1 ligand to metal ratio and an ionic nitrate. Erbium and yttrium nitrates give mononuclear ionic complexes $[Ln(NO_3)_2(27)_2]NO_3$ [93] whilst crystal structures of the neodymium complexes of
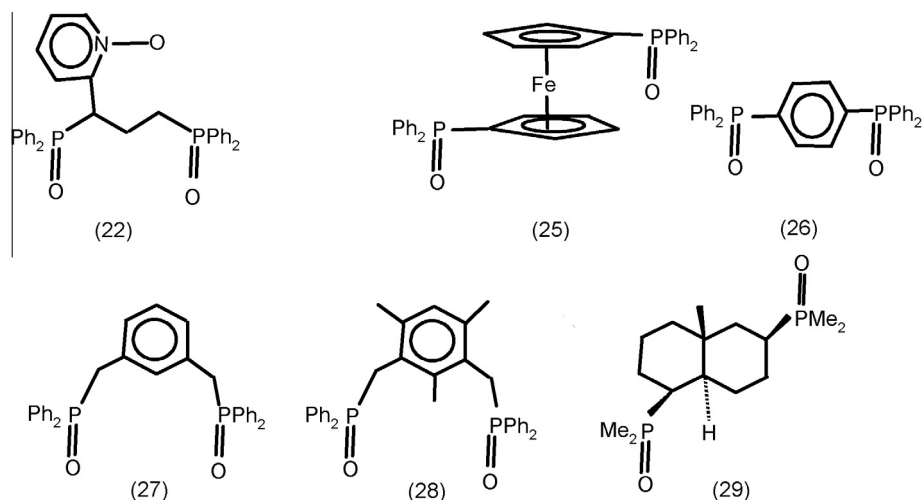
Fig. 6. The structures of compounds (22) and (25)–(29).

the mesitylene based *bis*-phosphine oxide (28) adopt different stoichiometries with 9-coordinate [Nd(NO$_3$)$_3$(28)·MeCN] and [Nd(NO$_3$)$_3$(28)·Me$_2$CO] formed[94]. The ^{31}P NMR spectra and conductivity measurements indicated that in acetonitrile ionisation occurs to a minor extent giving [Nd(NO$_3$)$_2$(28)]$^+$ (presumably solvated by acetonitrile). A major computational study of *bis*-phosphine oxide structures has been undertaken with the aim of directing a rational approach for the design of lanthanide extractants [95]. Whilst compounds such as (29) appear to have the most promise from a theoretical point of view, it and others amongst the most attractive compounds would be difficult to synthesise and compounds which are more readily accessible such as (30), Fig. 7, appear to be of the most potential practical use.

There has been extensive study of mixed NO PO ligands as potential extractants for use in f-element separation from main group and transition elements in nuclear fuels reprocessing. Many variants of the NOPOPO ligand (31) have been explored. For practical application as extractants hydrocarbon solubility is essential and lanthanide complexes of (31) R^1 = R^2 = R^3 = R^4 = Bz, 4-Me-C$_6$H$_4$, Et, Prop, Bu, Pn, Hx, Hp and Oct and (31) R^1 = R^3 = Ph, R^2 = R^4 = Bz, R^1 = R^3 = Ph, R^2 = R^4 = Me, R^1 = R^3 = Ph, R^2 = R^4 = Hx

and R^1 = R^3 = Ph, R^2 = R^4 = Oct have been prepared and their coordination complexes with lanthanide nitrates studied [96]. The structures are 9-coordinate with tridentate (31) in [Ln(NO$_3$)$_3$(31)] which have distorted tricapped trigonal prismatic or distorted monocapped square antiprismatic geometries. Complexes with a 2:1 ligand to metal ratio can also be formed and the structure of [Nd(31)$_2$(H$_2$O)$_2$](NO$_3$)$_3$) R^1 = R^2 = R^3 = R^4 = 4-Me-C$_6$H$_4$ has been determined with an approximately dodecahedral geometry. All of the compounds exhibited enhanced hydrocarbon solubilities compared to (31) R^1 = R^2 = R^3 = R^4 = Ph. The thermodynamics of the extraction of Am^{3+} and Eu^{3+} with (31) R^1 = R^2 = R^3 = R^4 = 2-ethylhexyl have been explored[97]. Both Am^{3+} and Eu^{3+} are extracted from aqueous nitric acid with two ligands associated with the metal nitrate in an exothermic process with a negative ΔS, with the NO weakly bonding to the metal in contrast to the crystallographically studied complexes. The compound (31) R^1 = R^2 = R^3 = R^4 = Cy has been studied and [Er(NO$_3$)$_3$(31)] was structurally characterised [98]. The structure shows that (31) acts as a tridentate ligand and that the nitrate ions are also bidentate. The incorporation of trifluoromethyl groups can increase solubility in fluorinated solvents and the coordination chemistry of (31)
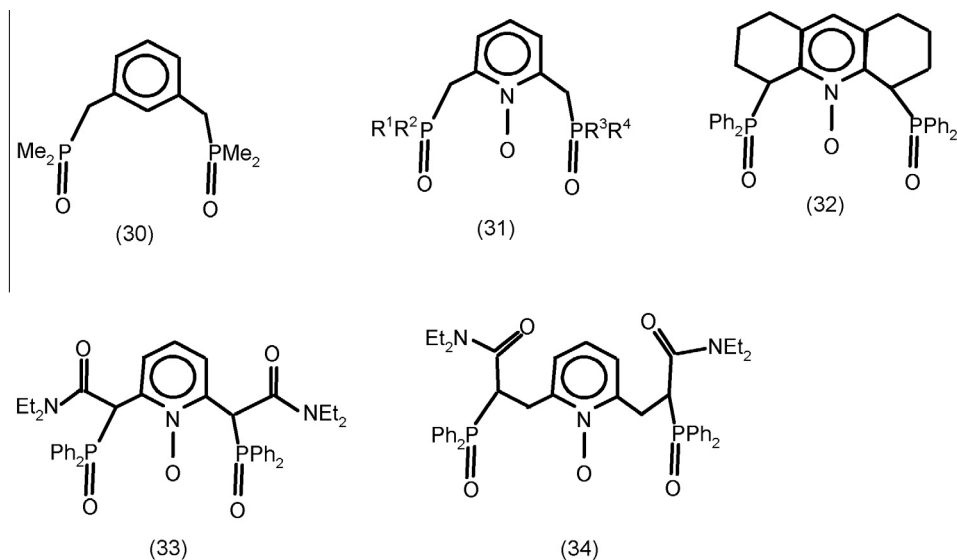

Fig. 7. The structures of compounds (30)–(34).

$R^1 = R^2 = R^3 = R^4 = $ 2-CF$_3$-C$_6$H$_4$ and 3,4-(CF$_3$)$_2$-C$_6$H$_3$ has been studied [99]. The 1:1 complexes [Ln(NO$_3$)$_3$(**31**)] are formed despite excess (**31**) being used in the synthesis. The ligands are tridentate towards lanthanide nitrates and the complexes have a distorted square capped antiprismatic geometry around the metal. Further refinements of the ligand structure involve a more rigid backbone in (**32**) where the compound chelates to the metal via PO, NO and bridges to a second metal via the second PO group [100]. The structures of the lanthanum and neodymium complexes show a 1:1 stoichiometry [Ln(NO$_3$)$_3$(**32**)]$_n$ with a polymeric chain in which each metal has a monocapped square antiprismatic coordination geometry. The potentially pentadentate (**33**) and (**34**) were studied as carbamoyl substituted phosphine oxides are used for extraction in nuclear fuels reprocessing [101]. The reaction between a 54:46 mixture of rac:meso (**33**) gave [Ln(NO$_3$)$_3$(**33**$_{R,S}$)] (Ln = Pr, Eu, Er) in which the metal is 9-coordinate with bidentate nitrates and (**33**) bound via both PO groups, the NO and one CO with the second amide carbonyl oxygen rotated away from the metal. With erbium nitrate two forms were crystallised with (**33**$_{R,S}$) and (**33**$_{S,S}$); [Er(NO$_3$)$_3$(**33**$_{R,S}$)]·Me$_2$CO is 9-coordinate with the carbamoyl oxygen atoms not bonded to the metal, whilst in [Er(NO$_3$)$_2$(**33**$_{S,S}$)(H$_2$O)](NO$_3$) (**33**) is tetradentate with the second CO H-bonded to the coordinated water molecule. Preliminary solvent extraction screening shows (**33**) to be an effective extractant for Eu^{3+} and Am^{3+} from nitric acid solutions. The introduction of a methylene group between the phosphoryl and pyridine N–oxide moieties in (**34**) gives rise to complexes in which the increased flexibility allows pentadentate coordination in the binuclear complex {[Pr(NO)$_3$)(**34**$_{R,S}$)(H$_2$O)]$_2$-μ-(**34**$_{R,R}$)}(NO$_3$)$_4$. Lanthanum and europium nitrate complexes of (**35**), Fig. 8, were isolated but could not be obtained in a form suitable for structural studies [102]. Solvent extraction studies indicate that the ligand has promise in nuclear fuels reprocessing.

The structure of the erbium nitrate complex of (**36**, X = O), [Er(NO$_3$)$_2$(**36**)](NO$_3$) as a methanol solvate shows the metal to be 8-coordinate with the furan oxygen atom not bonded to the metal despite computational analysis suggesting that there would be relatively little strain energy involved in it doing so [103]. With X = SO$_2$ (**36**) gives a 1:1 molecular complex [Pr(NO$_3$)$_3$(**36**)(MeOH)$_2$] in which the Pr ion is 10-coordinate with (**36**) bonding through one PO and one SO with the second PO H-bonded to the coordinated methanol molecule [104]. The related (**37** X = O) forms 1:1 complexes where it acts as a bidentate ligand via both PO groups in [Ln(NO$_3$)$_3$(**37**)(MeCN)] (Ln = Pr, Er) as acetonitrile solvates with a tricapped trigonal prismatic geometry about the metal [103]. The 2:1 complexes were obtained with difficulty but the structure of [Nd(NO$_3$)$_2$(**37**)$_2$](NO$_3$)$_2$ was determined and both (**37** X = O) were bidentate. With X = S (**37**) forms [Pr(NO$_3$)$_3$(**37**)(MeCN)] and [Pr(NO$_3$)$_3$(**37**)(H$_2$O)] with the S-atom not coordinated to the metal as expected [104]. The sulfone derivative (**37** X = SO$_2$) bonds as a tridentate ligand in [La(NO$_3$)$_3$(**37**)(H$_2$O)] and [Er(NO$_3$)$_3$(**37**)]·2MeCN with the reduced coordination number in the erbium complex being a consequence of the lanthanide contraction [104]. The ^{31}P NMR spectra of the La complex indicate that a dynamic equilibrium exists between free ligand and complexes of (**36**) and (**37**) in methanol. Solvent extraction studies showed that (**36** X = SO$_2$) was
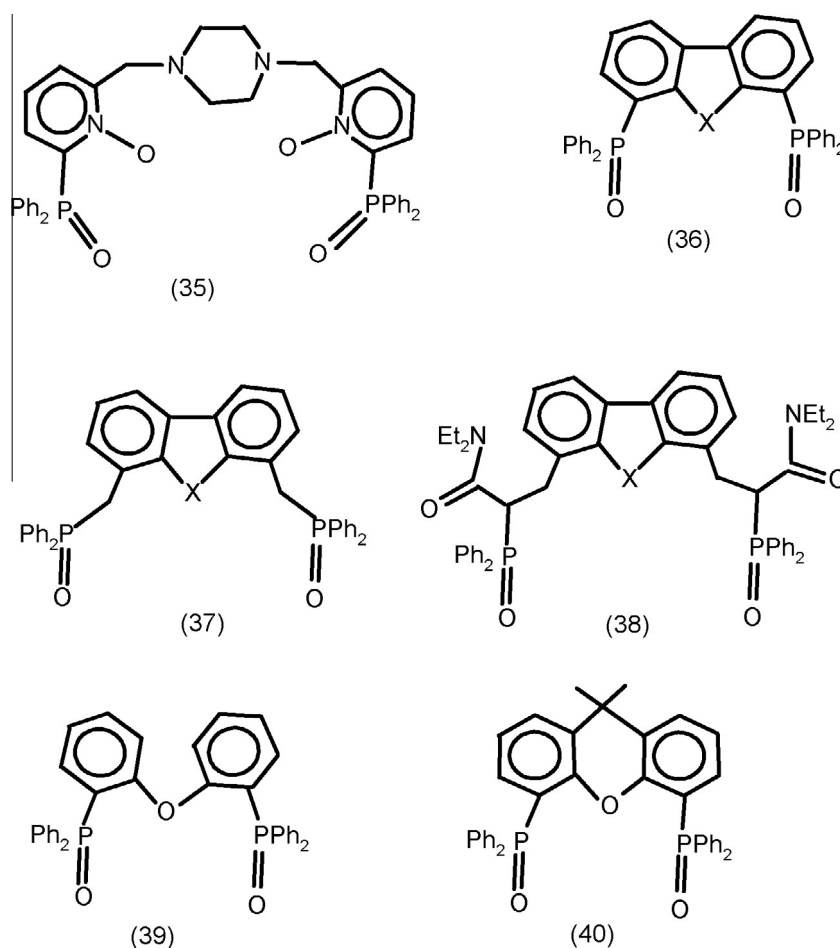

Fig. 8. The structures of compounds (**35**)–(**40**).

better performing than (**37** X = SO$_2$) [104] and that (**37** X = O) is a stronger extractant than (**36** X = O) [103]. Complexes of (**38** X = S) (Ln = La, Pr, Eu, Er, Lu) are tetradentate on the basis of infrared spectroscopy in [Ln(NO$_3$)$_3$(**38**)], whilst the coordination mode of (**38** X = SO$_2$) is unclear due to overlap of bands in the spectra [105]. The crystal structure with X = SO shows that in [Eu(NO$_3$)$_3$(**38**)], (**38**) bonds via both PO and the SO oxygen atoms with the amide carbonyl groups not bonded to the metal.

4.2. Complexes with lanthanide halides

The structures of a series of holmium chloride complexes of methylene bisphosphine oxides (R$_2$PO)$_2$CH$_2$ (R = 4Me-C$_6$H$_4$, Oct) have been examined in ethanol solution by EXAFS [106]. The chloride ions are not in the primary coordination sphere of the Ho^{3+} ion and the complexes are best formulated as [Ho(R$_2$P(O)CH$_2$P(O)R$_2$)$_2$(H$_2$O)$_4$]$^{3+}$ (R = 4Me-C$_6$H$_4$) and [Ho(R$_2$P(O)CH$_2$P(O)R$_2$)(H$_2$O)$_4$]$^{3+}$ (R = Oct). The shorter Ho-O(P) distances for R = Oct are explained as being due to the increased ligand basicity compared to the aromatic analogue. The ethylene bisphosphine oxide, ^{t}BuPhP(O)C$_2$H$_4$P(O)Ph^{t}Bu, gives a molecular 7-coordinate complex [CeCl$_3$(^{t}BuPhP(O)C$_2$H$_4$P(O)Ph^{t}Bu)$_2$] with a distorted pentagonal bipyramidal geometry about the metal [86]. The SmI$_3$ complex is considered to have the ionic structure[SmI$_2$(^{t}BuPhP(O)C$_2$H$_4$P(O)Ph^{t}Bu)$_2$]$^+$ I$^-$ on the basis of infrared spectroscopy and a cerium(IV) complex [CeCl$_4$(^{t}BuPhP(O)C$_2$H$_4$P(O)Ph^{t}Bu)] was also isolated but not structurally characterised. Neodymium chloride gives a polymeric network with 1,6-*bis*-diphenylphosphinohexane dioxide in which the metal has an octahedral geometry with *trans* chlorides and bridging phosphine oxides in [NdCl$_2$(Ph$_2$P(O)C$_6$H$_{12}$P(O)Ph$_2$)$_2$]Cl
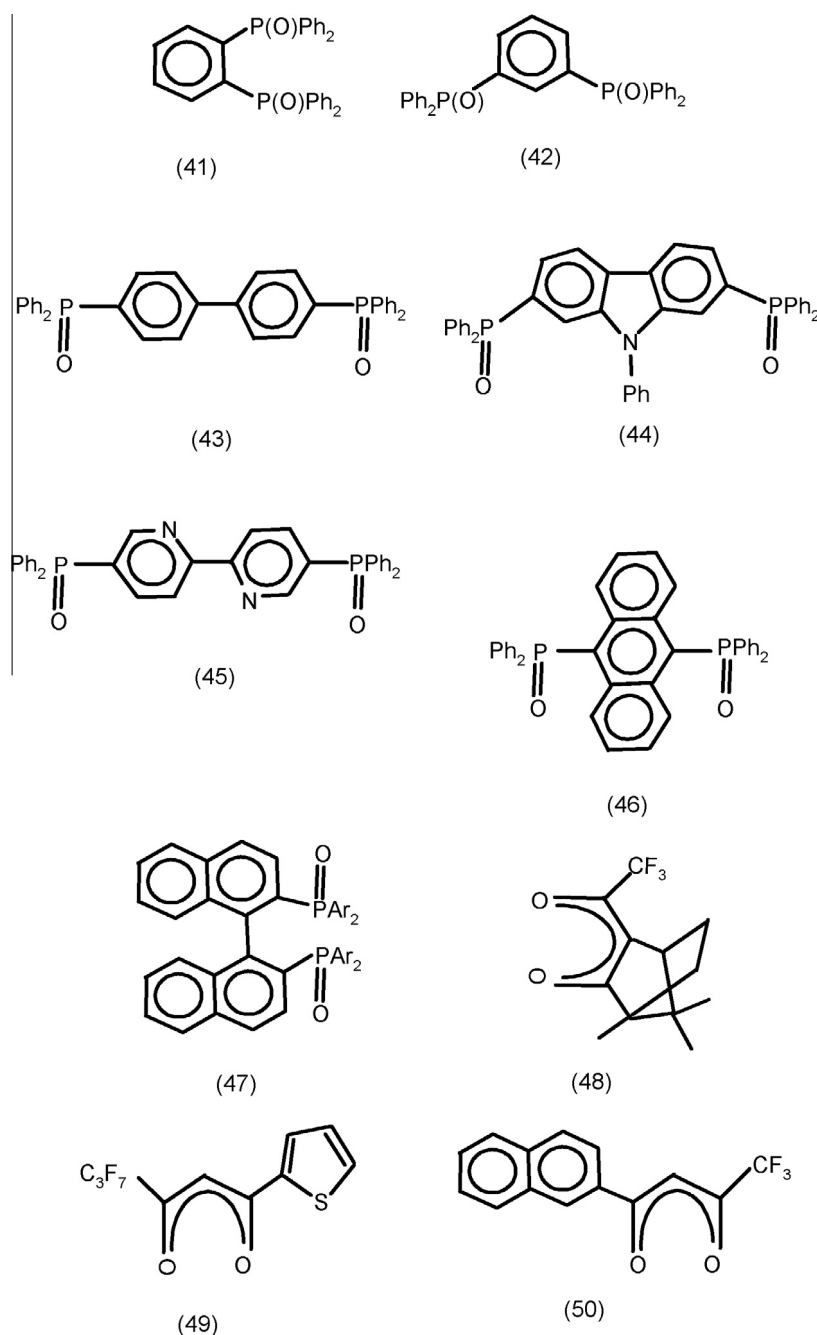

Fig. 9. The structures of compounds (**41**)–(**50**).

[90]. The erbium and lutetium complexes [LnCl$_2$(**25**)$_2$]Cl have an octahedral arrangement with *trans* chlorides [91]. The potentially tridentate ligands (**39**) and (**40**) react with hydrated lanthanide halides to give [LnCl$_2$(**39**)$_2$]Cl (Ln = Pr, Nd) in which the lanthanide ion has a distorted pentagonal bipyramidal arrangement with the chlorides in the axial positions and with one of the (**39**) ligands chelating through all three oxygen atoms [107]. The increased rigidity of the backbone in (**40**) prevents the ether oxygen atom bonding to the metal and the structures of [LaX$_2$(**40**)$_2$(H$_2$O)$_2$]X (X = Cl, Br) have a distorted square antiprismatic geometry with the square faces comprising the two halide ions and the four PO oxygen atoms. A europium chloride complex of (**37**) X = SO$_2$ has an empirical formula {[EuCl$_3$(**37**)]$_2$μ(**37**)} [104]. The single crystal X-ray structure shows each europium to be 7-coordinate with a tridentate (**37**), three chlorides and a PO from the bridging (**37**).

4.3. Complexes with lanthanide β-diketonates

Complexes which are based on β-diketonates allow the possibility to modify the structure of the anion as well as the phosphine oxide. This potential has been exploited primarily with the aim of developing light emitting devices based mainly on europium and terbium. Complexes of lanthanide hexafluoroacetylacetonates have been studied in depth with the phosphine oxide serving a number of roles. These include displacing water from the primary coordination sphere of the metal thereby reducing radiationless relaxation of excited states, and also as antennae for energy transfer from the ligand to the metal. In general the lanthanide hexafluoroacetylacetonates accommodate two PO groups, either as two monodentate or one bidentate ligand giving 8-coordinate structures.

The structures of a series of complexes of Eu(CF$_3$COCDCOCF$_3$)$_3$ with Ph$_2$P(O)CH$_2$P(O)Ph$_2$ (**19**), (**41**) and (**42**), Fig. 9, have been determined and show the europium to be square antiprismatic in [Eu(CF$_3$COCDCOCF$_3$)$_3$(**19**)], [Eu(CF$_3$COCDCOCF$_3$)$_3$(**41**)$_2$] and the polymeric [Eu(CF$_3$COCDCOCF$_3$)$_3$(**42**)$_2$] [108].

The photophysical properties of the complexes showed that [Eu(CF$_3$COCDCOCF$_3$)$_3$(**41**)$_2$] has a very sharp red emission with a wide stimulated emission cross-section. Complexes of (**26**), (**43**) and (**44**) are thermally stable decomposing only above 250 °C and the structures of the coordination polymers [Eu(CF$_3$COCHCOCF$_3$)$_3$(**26**)]$_n$, [Eu(CF$_3$COCHCOCF$_3$)$_3$(**43**)]$_n$ and [Eu(CF$_3$COCHCOCF$_3$)$_3$(**44**)]$_n$ are square
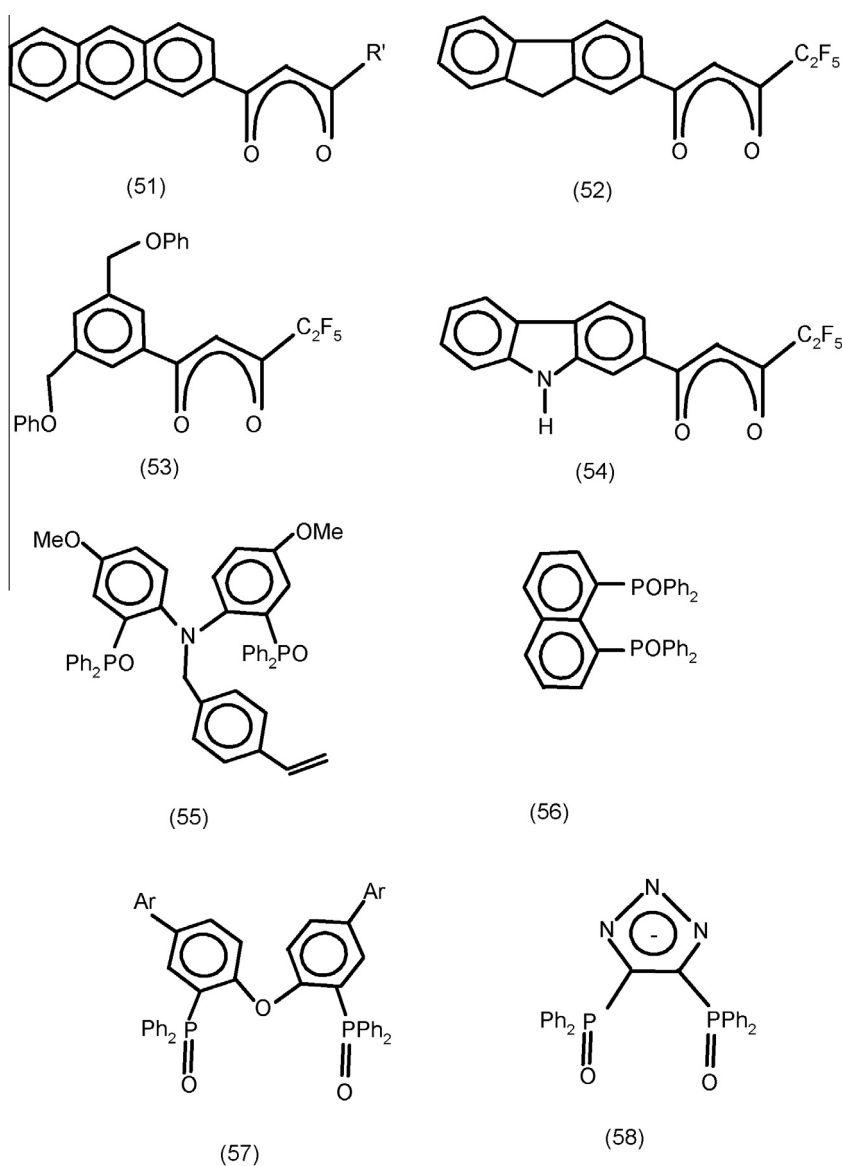
Fig. 10. The structures of compounds (**51**)–(**58**).

antiprismatic about the europium ion [109,110]. The complex of (**44**) in particular, has a high emission quantum yield of 83%. A polymeric complex, [Eu(CF$_3$COCHCOCF$_3$)$_3$(**45**)]$_n$ has a square antiprismatic geometry in which the phosphine oxide acts as a bridging ligand with the pyridyl nitrogen atoms not coordinated to the metal [111]. Both R and S forms of (**45**) are present in the crystal and there are short N...P distances. Intense red triboluminescence is observed from the 4f-4f transitions, $^5D_0$-^7F_J of the Eu^{3+} ion and the photoluminescent quantum yield is 61% on excitation at 380 nm in the crystal and 71% in acetone-d$_6$. The europium and terbium hexafluoroacetylacetonate complexes of (**46**) are dimeric with bridging phosphine oxides with a distorted square antiprismatic geometry about the metal and a strong π-π stacking in the solid state [112]. The wavelength difference between the fluorescence of (**46**) and the Eu ion is concentration dependent changing by 48 nm over a concentration range of 10^{-6} to 10^{-3} M. The emission from the europium ion remains constant over this concentration range, which gives the complex potential as a model for white light emitters. A similar temperature dependence of the emission was also observed. Mixed europium/terbium polymers [Ln(CF$_3$COCHCOCF$_3$)$_3$(**26**)]$_n$ have high emission quantum yields of 40% and a temperature sensitivity range of 100–500 K with green emission at 100 K and red at 300 K [113,114]. Circularly polarised luminescence was observed for the $^5D_0$-$^7F_1$ and $^5D_0$-$^7F_2$ transitions of [[Eu(CF$_3$COCHCOCF$_3$)$_3$(R-**47**)] (Ar = Ph) which were absent in the achiral form of the complex [115]. The chiral β-diketonate (**48**) gave crystals with two independent molecules in the unit cell – [Eu(D-**48**)$_3$(R-**47**)] and [Eu(D-**48**)$_3$(S-**47**)] (Ar = Ph) [116]. The single crystal X-ray structures show that the metal is 8-coordinated with a square antiprismatic geometry (as is the corresponding triphenylphosphine oxide complex [Eu(D-**48**)$_3$(Ph$_3$PO)$_2$]). The luminescent quantum yields are lower than in the corresponding hexafluoroacetylacetone derivatives due to effective vibrational relaxation. The bidentate ruthenocene derivative, (C$_5$H$_4$P(O)Ph$_2$)$_2$Ru forms an 8-coordinate [Eu(CF$_3$COCHCOCF$_3$)$_3$((C$_5$H$_4$P(O)Ph$_2$)$_2$Ru)$_2$] and is less readily oxidised than [Eu(CF$_3$COCHCOCF$_3$)$_3$((C$_5$H$_4$P(O)Ph$_2$)CpRu)$_2$] [60]. Unlike its counterpart with two monodentate ruthenocene phosphine oxides, it does not show changes in emission under potentiostatic polarisation due to restricted ring rotation making the formation of cationic ruthenium centres less favourable. The photoluminescence of a series of lanthanide hexafluoroacetylacetonate complexes of (**39**), [Ln(CF$_3$COCHCOCF$_3$)$_3$(**39**)], Ln = Nd, Eu, Tb, Yb has been studied and the structure of the gadolinium complex reported [117]. A synergistic effect was detected in the absorption properties between the ligands and a quantum yield of around 80% was found for the europium complex. Europium and ytterbium complexes [Ln(CF$_3$COCHCOCF$_3$)$_3$(**47**)], [Ln(**49**)$_3$(**47**)] and [Ln(**50**)$_3$(**47**)] (Ar = Ph) have been studied as high efficiency emitters [118]. The single crystal X-ray structure of [Ln(CF$_3$COCHCOCF$_3$)$_3$(S-**47**)] (Ar = Ph) shows a square antiprismatic geometry with two crystallographically independent molecules in the unit cell. [Eu(**49**)$_3$(**47**)] and [Eu(**50**)$_3$(**47**)] (Ar = Ph) show strong red emission even under ambient laboratory lighting. In the europium complex [Eu(**51**)$_3$(**47**)] (Ar = 4-CH$_3$-C$_6$H$_4$), Fig. 10, both the β-diketonate and phosphine oxide ligands act as antennae for the photoluminescent sensitisation of the Eu^{3+} ion [119].

Changing the R' substituent on (**51**) from phenyl to naphthyl to biphenyl increases the excitation window to the visible region allowing potential application to biomedical devices. The structures of [Eu(**52**)$_3$(**39**)] and [Eu(**52**)$_3$(**40**)], both prepared from [Eu(**52**)$_3$(H$_2$O)(EtOH)], are distorted square antiprisms in which the ether oxygen atoms of (**39**) and (**40**) are not coordinated to the europium ion [120]. The solid state quantum yield for the photoluminescence of the complex with (**40**) at 48% is significantly higher than that of (**39**) which has a yield of 28% due to more efficient energy transfer from the T$_1$ level of (**40**) to T$_1$ of (**52**). An

intense red emission under UV excitation is observed for [Eu(**53**)$_3$(**40**)] [121]. By attaching (EtO)$_3$SiC$_3$H$_6$NHC(O)- to the 2-position on the β-diketonate as a precursor the complex has been incorporated into a mesoporous solid matrix which also exhibits an intense red fluorescence with a quantum yield of 43%. Incorporation of the distorted square antiprismatic [Eu(**54**)$_3$(**40**)] into a polymethylmethacrylate film increases the photoluminescent quantum yield compared to the precursor complex from 47% to around 80% and the complex thus shows promise as a polymer based light emitting diode [122]. The replacement of water and ethanol in [(**15**)(H$_2$O)(EtOH)] (Ln = Eu, Tb) by (**39**) increases the photoluminescent quantum yield of the europium complex but reduced that of the terbium analogue [123]. The complexes [(**15**)(**39**)] are distorted square prisms with intermolecular π-π stacking of the phenyl rings of the β-diketonate groups and hydrogen bonding interactions between C–H and O/N atoms. Two europium containing copolymers were obtained from [Eu(**11**)$_3$(**55**)] and vinylcarbazole [124]. Spin coated polymer films have a strong red emission with quantum yields of 60%. The photophysical properties of the complex [Eu(**11**)$_3$(**56**)] show it has a quantum yield of 28% compared to 27% for the analogous [Eu(**11**)$_3$(Ph$_3$PO)$_2$] [125]. A series of complexes [Eu(**11**)$_3$(**57**)] have been prepared with a variety of Ar groups designed to increase the antenna effect of the ligands [126]. Quantum yields of up to 86% were found and the enhanced solubility of many of the complexes allowed the formation of spin coated single layer red light emitting devices.

4.4. Complexes with miscellaneous lanthanide salts

The structure of the complex between Eu(ClO$_4$)$_3$ and Ph$_2$P(O)CH$_2$P(O)Ph$_2$, (**19**), has and empirical formula [Eu(**19**)$_4$](ClO$_4$)$_3$·2H$_2$O in which the europium ion is 8-coordinate with a distorted square antiprismatic geometry[127]. With trifluoromethane sulfonates lanthanum forms a similar cation in [La(**19**)$_4$](OTf)$_3$·1.5H$_2$O whilst the smaller lutetium can only accommodate three phosphine oxides in [Lu(**19**)$_3$(H$_2$O)](OTf)$_3$ which has a distorted pentagonal bipyramidal geometry with the water occupying an equatorial position [128]. The electrospray mass spectra show that [La(**19**)$_3$]$^{3+}$ is the most abundant ion in the gas phase and that the expected [La(**19**)$_4$]$^{3+}$ whilst present, is at lower abundance. Solution ^{31}P NMR evidence indicates that (**19**) and (**41**) coordinate to a variety of lanthanum aryloxides, La(OAr)$_3$
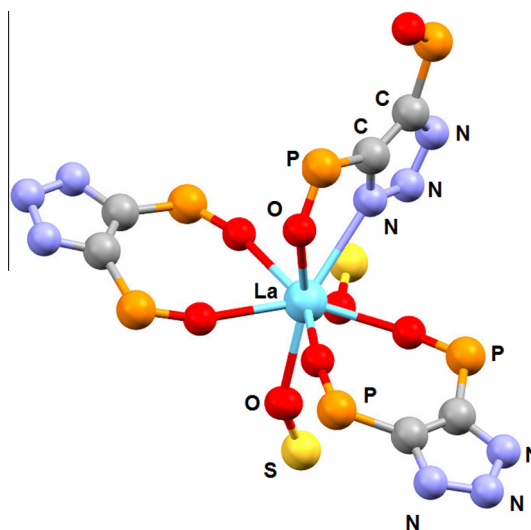

Fig. 11. The structure of [La(**58**)$_3$(DMSO)$_2$] (hydrogen and carbon atoms omitted for clarity) Reproduced using coordinates from Ref. [130].

and that catalytic amounts of the phosphine oxides activated the catalytic Mannich reaction[129]. A series of lanthanide complexes of the anionic ligand (**58**), [Ln(**58**)$_3$·nH$_2$O] and [Ln(**58**)$_3$(Phen)]·nH$_2$O have been prepared and the structures of [Ln(**58**)$_3$(DMSO)$_2$]·nH$_2$O reported for Ln = La, Ce, Nd, Sm and Gd for which the geometries are distorted trigonal dodecahedral [130]. The structures show that (**58**) adopts both PO, PO and PO, N chelating modes shown in Fig. 11.

The ^{31}P NMR spectra show that the unsymmetrical coordination is retained in solution. The complexes with 1,10-phenanthroline show higher photoluminescent quantum yields. The tetrazolate anion, (**59**), Fig. 12, forms complexes [Eu(**59**)$_3$(**39**)]·5H$_2$O which have increased photoluminescent quantum yields compared to [Eu(**59**)$_3$]·nH$_2$O [131].

5. Ligands with three or more PO groups

The tripodal ligands CH(CH$_2$P(O)Ar$_2$)$_3$ (Ar = Ph, 4-MeC$_6$H$_4$, 2-MeC$_6$H$_4$, 2,5-Me$_2$C$_6$H$_3$) form insoluble monomeric complexes [Y(NO$_3$)$_3$(CH(CH$_2$P(O)Ar$_2$)$_3$)] which have a distorted tricapped trigonal-prismatic structure [88]. The complexes are soluble in the presence of excess ligand and the ^{31}P NMR spectra indicate the presence of at least four different complexes in solution. The related MeC(CH$_2$P(O)Ph$_2$)$_3$ forms polymeric complexes with lanthanide nitrates in which the phosphine oxide chelates forming an 8-membered ring with two arms, and bridges to another lanthanide centre with the other [132]. The CMPO substituted triphenoxymethane (**60**) forms complexes with lanthanide nitrates in
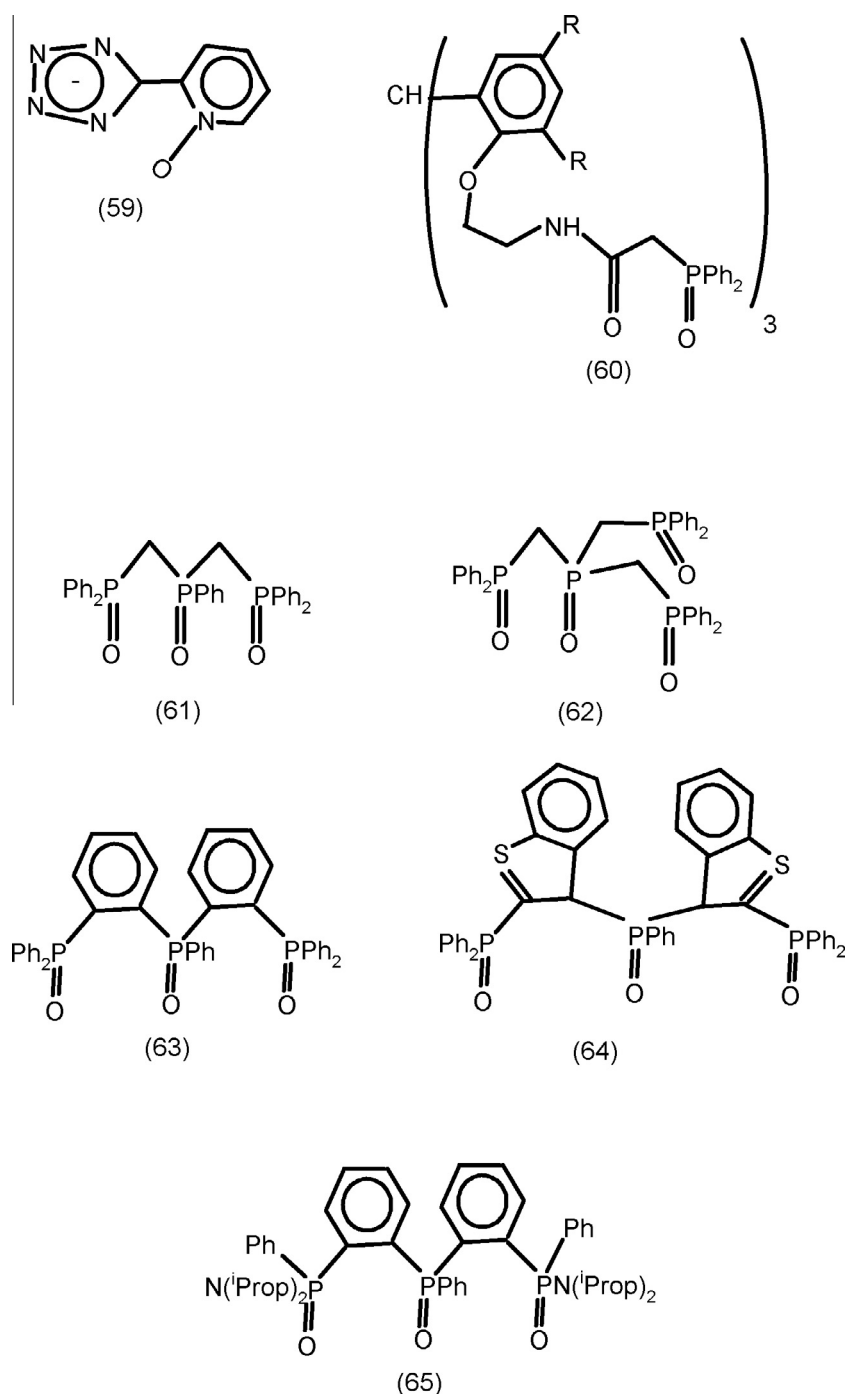

Fig. 12. The structures of compounds (**59**)–(**65**).

which all three CMPO arms bind to the metal in a bidentate manner [133]. The 1:1 complexes contain two cations [Nd(NO$_3$)(60)]$^{2+}$ and [Nd(NO$_3$)(H$_2$O)(60)]$^{2+}$ with [Nd(NO$_3$)$_5$]$^{2-}$ counterions. Extraction studies indicate that (60) is selective in extracting actinide over lanthanide ions. The extraction of Nd^{3+} from nitric and hydrochloric acid with the tri- and tetra-phosphine oxides (61) and (62) has been investigated [134]. It was found that mole ratios of Nd:(61) of 1:3 were most effective for extraction whilst 1:1 or 1:2 ratios of Nd:(62) were effective for the tetraphosphine oxide. The triphosphine oxides (63) and (64) form [Eu(CF$_3$-COCHCOCF$_3$)$_3$(63)] and [Eu(CF$_3$COCHCOCF$_3$)$_3$(64)] which have distorted capped square antiprismatic structures [135]. The complexes have emission quantum yields above 60% in acetone-d$_6$. Europium chloride complexes of (65) have been characterised as [EuCl$_3$(65)] and [EuCl$_2$(65)$_2$]Cl [136]. The structure of [EuCl$_3$(65)] is a distorted *fac*-octahedron which is retained in solution. In solution [EuCl$_2$(65)$_2$]Cl converts to [EuCl$_3$(65)], the process reaching an equilibrium conversion of about 80% after 120 h. Incorporation of (65) into a polymer film was found to have potential as

a luminescent probe for the detection of europium in aqueous solution. An NMR study of CMPO substituted calix[4]arene derivatives coordinate with lanthanide perchlorates differently depending on whether the phosphine oxide is attached to the wide or narrow rim [137]. Polymeric complexes are formed by (66) (X = OMe, OProp, Y = NHCOCH$_2$P(O)Ph$_2$, n = 4), Fig. 13, where the phosphine oxide is located on the wide rim, whilst (67) (X = ^{t}Bu, Y = OC$_3$H$_6$NHCOCH$_2$P(O)Ph$_2$, n = 4) with the phosphorus substituent on the narrow rim, forms well defined monomeric complexes in which all four arms act in a bidentate manner. Calculations indicate that for La^{3+} and Yb^{3+} ions a square antiprismatic geometry is the most stable. Extraction studies using (67) (X = ^{t}Bu, Y = OCH$_2$P(O)Me$_2$, n = 4) indicate that 1:2 complexes are formed with 4-benzoyl-3-phenyl-5-isoxazolones, (15), during the extraction process [138].

Analysis of the NMR spectra of the 1:1 complex [(15)(67)] (Ln = Eu) indicates that all four PO groups bind to the metal. Weak extraction of lanthanide ions is found for (67) (X = ^{t}Bu, Y = OCH$_2$P(O)Me$_2$, n = 4) in the absence of other reagents [139]. The crystal
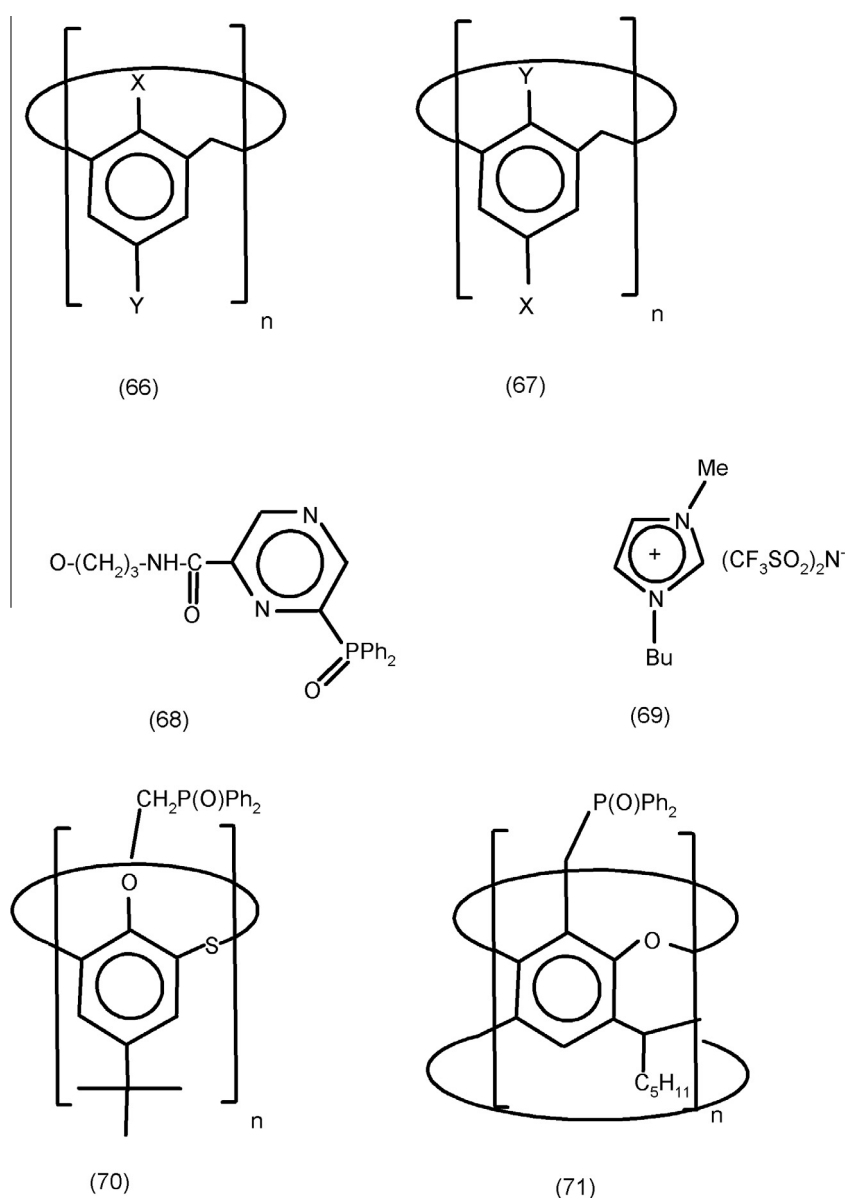

Fig. 13. The structures of compounds (66)–(71).

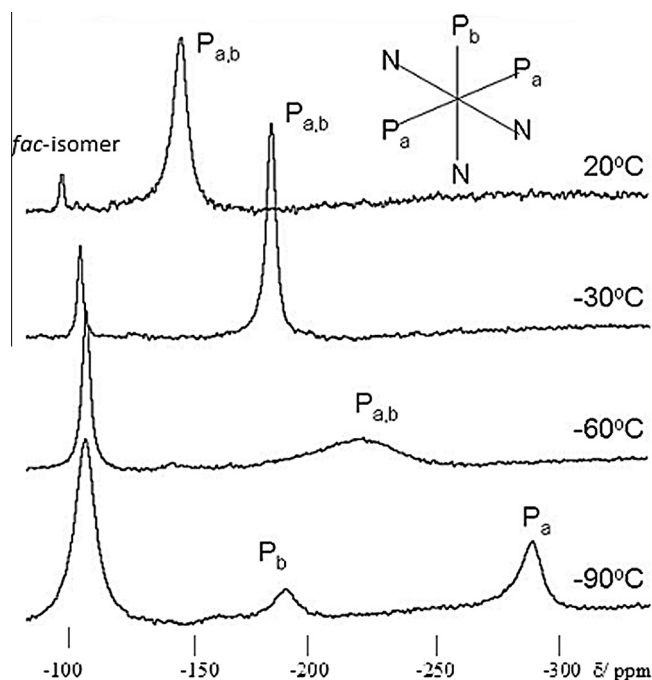Fig. 14. The variable temperature ^{31}P NMR spectra of [Er(NO$_3$)$_3$(^{i}Bu$_3$PO)$_3$].

structure of [La(67)(H$_2$O)$_5$](ClO$_4$)$_3$ shows a 9-coordinate structure with all four PO groups bonded to the lanthanum ion and four water molecules above the macrocycle with the fifth inside the cavity formed by the OCH$_2$P(O)Me$_2$ arms. The *tert*-octyl substituted (67) (X = -CMe$_2$CH$_2$CMe$_3$, Y = OCH$_2$P(O)Me$_2$, n = 4) on the basis of luminescence titrations, forms 1:1 and 1:2 complexes in solution [140]. The 1:1 complex, isolated for europium, has the empirical formula EuCl$_2$(OH)(67)(H$_2$O)$_4$ with at least one water molecule not directly bonded to the metal. No structural data were available for the compound. Extraction of lanthanide nitrates by (67) (X = ^{t}Bu, Y = OCH$_2$P(O)Me$_2$, n = 4) in which the wide rim also bears an alkyl halide group –(CH$_2$)$_5$Cl or –(CH$_2$)$_6$Cl, has been reported [141]. Whilst the presence of the chloroalkyl groups reduced the extraction efficiency marginally compared to the unsubstituted calix[4]arene, it offers the potential of tethering the extractant to

a solid substrate. The coordination of the pyrazine functionalised (67) (X = ^{t}Bu, Y = (68), n = 4) in the ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl) imide (69) has been studied [142]. Lanthanide ions form 1:1 complexes in which two arms bind via CO, aromatic N-atom and PO whilst the other two remain uncoordinated. The complex formation with Eu^{3+} is exothermic with an increase in entropy due to the displacement of water from the coordination sphere of the metal. Structures of the monocapped square antiprismatic La and Nd complexes of the thiacalix[4]arene (70), [Ln(NO$_3$)$_2$(OH)(70)] have been reported [143]. All four PO groups are bonded to the lanthanide ions with nitrates coordinated above the macrocycle and the hydroxide ion in the cavity formed by the four OCH$_2$P(O)Ph$_2$ arms. The sulfur atoms are, as expected, not coordinated to the metal ions.

The reaction of [Tb(DMSO)$_8$](OTf)$_3$ with the resorcinarene (71) gives the polymeric complex, [Tb$_2$(71)(DMSO)$_8$](OTf)$_6$ in which [Tb(71)(DMSO)$_4$(OTf)]$^{2+}$ units are linked in a chain. The terbium ions have a 7-coordinate pentagonal bipyramidal arrangement comprising two PO groups in axial positions with the equatorial plane made up of one OTf$^-$ and four DMSO [144]. Analysis of the luminescence spectra indicates that there is no electronic interaction between the two terbium centres in the polymer.

The potentially hexadentate (67) (X = ^{t}Bu, Y = OCH$_2$P(O)Me$_2$, n = 6) forms two types of complex with lanthanide perchlorates [145]. Complexes of 1:1 and 1:2 stoichiometry Ln(67)(ClO$_4$)$_3$·xH$_2$O (n = 3 or 6 depending on Ln) and Ln(67)$_2$(ClO$_4$)$_3$·xH$_2$O (n = 3, 4, 5 depending on Ln) have been isolated and the infrared spectra indicate the presence of both coordinated an ionic perchlorate whilst NMR spectra indicate that at least four isomers are present in solution.

6. The application of ^{31}P NMR Spectroscopy in the analysis of lanthanide phosphine oxide complexes

The use of ^{31}P NMR spectroscopy in the characterisation of phosphine oxide complexes is routine. The paramagnetic shifts for most of the ions mean that the signals appear a long way, often several hundred ppm, from their normal position in the free ligand or in diamagnetic complexes. In addition, the large shift in resonance position is often accompanied by considerable paramagnetic line broadening. Line widths up to several kHz are not uncommon, particularly for middle to late lanthanides. This effect can also be
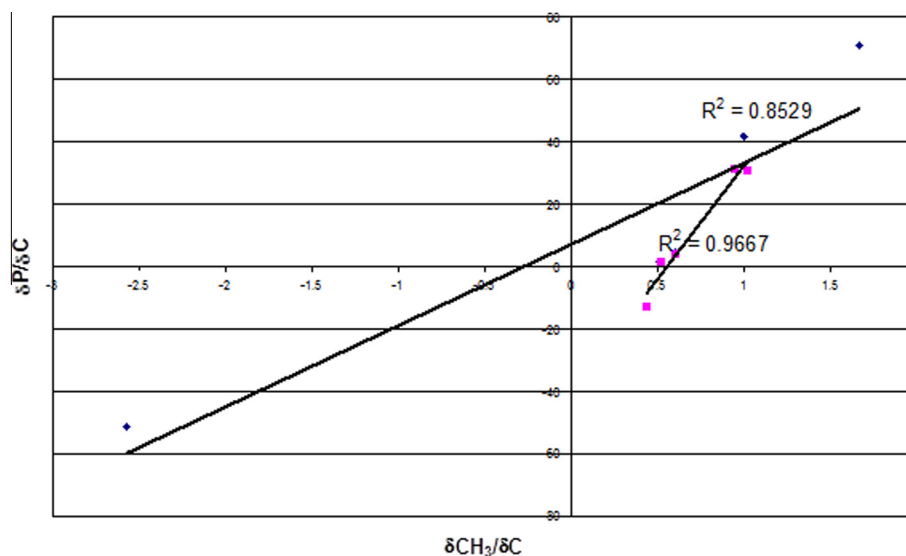

Fig. 15. A shift ratio plot for [Ln(NO$_3$)$_3$(^{t}Bu$_3$PO)$_2$].

compounded if the complexes undergo exchange processes on the NMR timescale This can often lead to a considerable investment in spectrometer time to accumulate good quality spectra. The spectra of individual complexes are generally less informative than in d-block metal phosphine complexes for instance, although recording spectra at low temperature can sometimes slow dynamic processes sufficiently to allow static spectra to be observed. An example is shown in Fig. 14 where the presence of *fac* and *mer*-isomers of $[Er(NO_3)_3(^iBu_3PO)_3]$ are clearly seen. The *mer*-isomer is fluxional at 20 °C whilst at −90 °C the signals from the two phosphorus environments are seen. In many cases only single resonances are observed, either because low temperature measurements were not performed or because the phosphorus environments exchange so rapidly that static spectra cannot be observed. Under these circumstances useful information can still be extracted if spectra from complexes of all the lanthanides, or a substantial part of the series are obtained. Analysis of lanthanide induced shifts can give an insight into the distribution of structures across the series. Methods have been developed for the analysis of one, two or three nuclei [146,147]. The strict application of the one and two nucleus methods makes assumptions on the geometry of the complexes whilst the three nucleus treatment (shift ratio plots) is a model independent, although finding three nuclei which are readily assignable is sometimes problematic. An example of a shift ratio plot is shown in Fig. 15 for $[Ln(NO_3)_3(^tBu_3PO)_2]$. Here the presence of two lines in the plot of dP/dC vs dCH_3/dC indicates the presence of two types of complex in solution, a finding in accord with the X-ray crystallography results.

7. Concluding remarks

The coordination chemistry of phosphine oxides continues to be of interest in a number of fields and this activity is likely to continue. The ability to incorporate a wide variety of groups into the structures of the ligands effectively gives enormous scope to the fine tuning of the properties of the resulting complexes. The majority of the complexes studied are for the trivalent metals and there would appear to be more work to be done particularly on complexes of divalent lanthanides. Studies on group(II) cations show that complexes can be formed with monodentate and bidentate phosphine oxides [148]. It would be reasonable to suppose the Eu^{2+} and possibly other accessible Ln^{2+} such as Sm and Yb might form similar complexes.

References

[1] E. Giesbrecht, Pure Appl. Chem. 51 (1979) 925.
[2] S. Mishra, Coord. Chem. Rev. 252 (2008) 1996.
[3] D.G. Giheany, Chem. Rev. 94 (1994) 1339.
[4] D.B. Chesnut, J. Am. Chem. Soc. 120 (1998) 10504.
[5] D.B. Chesnut, J. Am. Chem. Soc. 121 (1999) 2335.
[6] D.L. Bryce, K. Eichele, R.E. Wasylishen, Inorg. Chem. 42 (2002) 5085.
[7] A.G. Cook, G.W. Mason, J. Org. Chem. 37 (1972) 3342.
[8] J.C. Bollinger, R. Houriet, C.W. Kern, D. Perret, J. Weber, T. Yvernault, J. Am. Chem. Soc. 107 (1985) 5352.
[9] N. De Silva, F. Zahariev, B.P. Hay, M.S. Gordon, T.L. Windus, J. Phys. Chem. A 119 (2015) 8765.
[10] A.M.G. Massabni, M.D.R. Gibran, O.A. Serra, Inorg. Nucl. Chem. Lett. 14 (1978) 419.
[11] L. Deakin, W. Levason, M.C. Popham, G. Read, M. Webster, J. Chem. Soc. Dalton Trans. (2000) 2439.
[12] M. Bosson, W. Levason, T. Patel, M.C. Popham, M. Webster, Polyhedron 20 (2001) 2055.
[13] A. Bowden, A.W.G. Platt, K. Singh, Polyhedron 42 (2012) 30.
[14] A. Bowden, S.J. Coles, M.B. Pitak, A.W.G. Platt, Polyhedron 68 (2014) 258.
[15] A. Bowden, P. Horton, A.W.G. Platt, Inorg. Chem. 50 (2011) 2553.
[16] A. Bowden, S.J. Coles, M.B. Pitak, A.W.G. Platt, Inorg. Chem. 51 (2012) 4379.
[17] C.A. Tolman, Chem. Rev. 77 (1977) 345.
[18] A.P. Hunter, A.M.J. Lees, A.W.G. Platt, Polyhedron 26 (2007) 4865.
[19] V.K. Manchanda, K. Chander, P. Singh, G.M. Nair, J. Inorg. Nucl. Chem. 39 (1977) 1039.
[20] R.V. Fox, R.D. Ball, P. de Harrington, H.W. Rollins, J.J. Jolly, C.M. Wai, J. Supercrit. Fluids 31 (2004) 273.
[21] N. Anitha, D.N. Ambare, D.K. Singh, H. Singh, P.K. Mohapatra, Chem. Eng. Res. Des. 98 (2015) 89.
[22] X. Sun, Y. Ji, L. Guo, J. Chen, D. Li, Sep. Purif. Technol. 81 (2011) 25.
[23] T.S. Grimes, P.R. Zalupski, L.R. Martin, J. Phys. Chem. B 118 (2014) 12725.
[24] W. Levason, E.H. Newman, M. Webster, Polyhedron 19 (2000) 2697.
[25] S. Xu, M. Liu, H.-L. Han, Z.-F. Li, Q.-H. Jin, W. Su, Y.-Y. Chen, J.-Y. Yao, Polyhedron 85 (2015) 69.
[26] Z. Yanhui, P. Jianbo, P. Juan, G. Xiaotian, W. Yunyou, S. Bo, J. Rare Earths 24 (2006) 146.
[27] A.T. Thames, F.D. White, L.N. Pham, K.R. Xiang, R.E. Sykora, Acta Crystallogr. Sect E Struct. Rep. online 68 (2012) m1530.
[28] M. Ul-Haque, C.N. Caughlan, F.A. Hart, R. van Nice, Inorg. Chem. 10 (1971) 115.
[29] A.W.G. Platt, K. Singh, J. Mol. Struct. 1111 (2016) 180.
[30] D.S. Amenta, S.N. Sparks, J.W. Gilje, F.T. Edelmann, A. Fischer, S. Blaurock, Z. Anorg, Allg. Chem. 631 (2015) 69.
[31] Y. Sano, J. Karino, T. Koyama, H. Funasaka, J. Alloys Compd. 303–304 (2000) 151.
[32] S.A. Ansari, P.K. Mohapatra, D.R. Raut, M. Kumar, B. Rajeswari, V.K. Manchanda, J. Membr. Sci. 337 (2009) 304.
[33] G. Boehme, G. Wipff, Inorg. Chem. 41 (2002) 727.
[34] C.-Z. Wang, W.-Q. Shi, J.-H. Lan, Y.-L. Zhao, Y.-Z. Wei, Z.-F. Chai, Inorg. Chem. 52 (2013) 10904.
[35] P.-Y. Jiang, Y. Ikeda, M. Kumagai, J. Nucl. Sci. Technol. 31 (1994) 491.
[36] R. Babecki, A.W.G. Platt, Inorg. Chim. Acta 171 (1990) 25.
[37] S. Quizem, D. Rosario-Amorin, D.A. Dickie, R.T. Paine, A. de Bettencourt-Dias, B.P. Hay, J. Podiat, L.H. Delmau, J. Chem. Soc. Dalton Trans. 43 (2014) 8368.
[38] S.L. Pailloux, C.E. Shirima, A.D. Ray, E.N. Duesler, K.A. Smith, R.T. Paine, J.R. Klaehn, M.E. McIlwain, B.P. Hay, J. Chem. Soc. Dalton Trans. (2009) 7486.
[39] S.L. Pailloux, D. Rosario-Amorin, M. Chakravarty, J.-M. Camus, K.A. Smith, E.N. Duesler, D.A. Dickie, R.T. Paine, K.K. Klausmeyer, J.A. Padron, B.P. Hay, L.H. Delmau, Z. Anorg. Allg. Chem. 639 (2013) 1101.
[40] L. Prodi, M. Montalti, N. Zaccheroni, G. Pickaert, L. Charbonniere, R. Ziessel, New J. Chem. 27 (2003) 134.
[41] L. Charbonniere, R. Ziessel, M. Montalti, L. Prodi, C. Boehme, G. Wipff, J. Am. Chem. Soc. 124 (2002) 7779.
[42] S.L. Pailloux, C.E. Shirima, E.N. Duesler, K.A. Smith, R.T. Paine, Polyhedron 30 (2011) 2746.
[43] M.J.D. Champion, W. Levason, G. Reid, J. Fluorine Chem. 157 (2014) 19.
[44] N.J. Hill, L.-S. Leung, W. Levason, M. Webster, Acta Crystallogr. C 58 (2002) 295.
[45] N.J. Hill, L.-S. Leung, W. Levason, M. Webster, Inorg. Chim. Acta 343 (2003) 169.
[46] N.J. Hill, W. Levason, M.C. Popham, G. Reid, M. Webster, Polyhedron 21 (2002) 445.
[47] A.M.J. Lees, A.W.G. Platt, Polyhedron 67 (2014) 368.
[48] Y.-C. Chen, J.-L. Liu, L. Ungur, J. Lui, Q.-W. Wen, L.-F. Wang, Z.-P. Ni, L.F. Chibotaru, X.-M. Chen, M.L. Tong, J. Am. Chem. Soc. 138 (2016) 2829.
[49] M.J. Glazier, W. Levason, M.L. Matthews, P.L. Thornton, M. Webster, Inorg. Chim. Acta 357 (2004) 1083.
[50] H.-K. Wang, M.-J. Zhang, X.-Y. Jing, J.-T. Wang, R.-J. Wang, H.-G. Wang, Inorg. Chim. Acta 163 (1989) 19.
[51] A. Bowden, A.M.J. Lees, A.W.G. Platt, Polyhedron 91 (2015) 110.
[52] A. Bowden, A.W.G. Platt, K. Singh, R. Townsend, Inorg. Chim. Acta 363 (2010) 243.
[53] J.-C. Berthet, M. Nierlich, M. Ephritikhine, Polyhedron 22 (2002) 3475.
[54] J. Feng, L. Zhou, S.-Y. Song, Z.-F. Li, W.-Q. Fan, L.-N. Sun, Y.-N. Yu, H.-J. Zhang, Dalton Trans. (2009) 6593.
[55] A. Monguzzi, R. Turbino, F. Meinardi, A.O. Biroli, M. Pizzotti, F. Demartin, F. Quochi, F. Cordella, M.A. Loi, Chem. Mater. 21 (2009) 128.
[56] A.O. Biroli, M. Pizzotti, P. Illiano, F. Demartin, Inorg. Chim. Acta 366 (2011) 254.
[57] Y. Hasegawa, T. Ohkubo, T. Nakanishi, A. Kobayashi, T. Kato, H. Ito, K. Fushimi, Eur. J. Inorg. Chem. (2013) 5911.
[58] O. Pietraszkiewcz, S. Mal, M. Pietraszkiewcz, M. Maciejczyk, I. Czerski, T. Borowiak, G. Dutkiewicz, L. Pennick, J. Beeckman, K. Neyts, J. Photochem. Photobiol. A 250 (2012) 85.
[59] J.V. Vicente, A. Mlonka, H.Q. Nimal Gunaratne, M. Szadzba-Kwasny, P. Nockeman, Chem. Commun. 48 (2012) 6115.
[60] Y. Hasegawa, N. Sato, Y. Hirai, Y. Kitagawa, A. Kobayashi, M. Kato, T. Seki, H. Ito, K. Fushima, J. Phys. Chem. 119 (2015) 4825.
[61] H.F. Brito, O.L. Malta, M.C.F.C. Felinto, E.E.S. Teotonio, J.F.S. Menezes, C.F.B. Silva, C.S. Tomiyama, C.A.A. Carvalho, J. Alloys Compd. 344 (2002) 293.
[62] E.E.S. Teotonio, G.M. Fett, H.F. Brito, W.M. Faustino, G.F. de Sa, M.C.F.C. Felinto, R.H.A. Santos, J. Lumin. 128 (2008) 190.
[63] H. Xu, K. Yin, W. Huang, Chem. Eur. J. 13 (2007) 10281.
[64] H. Xu, W. Huang, J. Photochem. Photobiol. A 217 (2011) 213.
[65] E.E.S. Teotonio, F.A. Silva, D.K.S. Pereira, L.M. Santo, H.F. Brito, W.M. Faustino, M.C.F.C. Felinto, R.H.A. Santos, R. Morento-Fuquen, A.R. Kenedy, D. Gilmore, Inorg. Chem. Commun. 13 (2010) 1391.
[66] R. Pavithran, N.S. Saleesh Kumar, B. Biju, M.L.P. Reddy, S.A. Junior, R.O. Freire, Inorg. Chem. 45 (2006) 2184.
[67] Z. Li, J. Yu, L. Zhou, R. Deng, H. Zhang, Inorg. Chem. Commun. 12 (2009) 151.
[68] Z. Li, J. Yu, L. Zhou, H. Zhang, R. Deng, Inorg. Chem. Commun. 11 (2008) 1284.

[69] X. Li, Z. Si, C. Pan, L. Zhou, X. Li, J. Tang, H. Zhang, Inorg. Chem. Commun. 12 (2009) 675.
[70] R.P. Feazell, J.B. Gary, J.A. Kautz, K.K. Klausmeyer, C.W. Wong, M. Zancanella, Acta Crystallogr. E 60 (2004) m532.
[71] L.M. Pham, A.T. Thames, F.D. White, K.R. Xiang, R.E. Sykora, Acta Crystallogr. E 68 (2012) m1531.
[72] J. Fawcett, A.W.G. Platt, D.R. Russell, Polyhedron 21 (2002) 287.
[73] J. Fawcett, A.W.G. Platt, D.R. Russell, Inorg. Chim. Acta 274 (1998) 177.
[74] J.A.W.G. Platt, J. Fawcett, R.S. Hughes, D.R. Russell, Inorg. Chim. Acta 295 (1999) 146.
[75] Z. Spinchal, J. Pinkas, N. Necas, Polyhedron 48 (2012) 99.
[76] W.R. Lee, D.W. Ryu, J.W. Lee, J.H. Yoon, E.K. Koh, C.S. Hong, Inorg. Chem. 49 (2010) 4723.
[77] I.A. Ibarra, T.W. Hesterberg, B.J. Holliday, V.M. Lynch, S.M. Humphrey, Dalton Trans. 41 (2012) 8003.
[78] I.A. Ibarra, J.W. Yoon, J.-S. Chang, S. Kyoung, V.M. Lynch, Inorg. Chem. 51 (2012) 12242.
[79] Z.-J. Lin, Z. Yang, T.-F. Liu, Y.-B. Huang, R. Cao, Inorg. Chem. 51 (2012) 1813.
[80] P.L. Arnold, J.-C. Buffet, R. Blaudeck, S.S. Sujecki, C. Wilson, Chem. Eur. J. 15 (2009) 8241.
[81] P.L. Arnold, J.-C. Buffet, R. Blaudeck, S.S. Sujecki, A.J. Blake, C. Wilson, Angew. Chem. Int. Ed. 47 (2008) 6033.
[82] L. Beverina, M. Crippa, M. Sassi, A. Monguzzi, F. Meinardi, R. Tubina, G.A. Pagani, Chem. Commun. (2009) 5103.
[83] A.M.J. Lees, A.W.G. Platt, Inorg. Chem. 42 (2003) 4673.
[84] A.G. Matveeva, A.V. Vologzhanina, W.I. Goryunov, R.R. Aysin, M.P. Pasechnik, S.V. Mateev, I.A. Godovikov, A.M. Safinulina, V.K. Brel, Dalton Trans. 45 (2016) 5126.
[85] Z. Spichal, M. Necas, J. Pinkas, J. Novosad, Inorg. Chem. 43 (2004) 2776.
[86] K. Koide, A. Sakamoto, T. Imamoto, T. Tanase, Y. Yamammoto, J. Alloys Compd. 192 (1993) 211.
[87] R.T. Paine, E.M. Bond, S. Parveen, N. Donhart, E.N. Duesler, K.A. Smith, H. Noth, Inorg. Chem. 41 (2002) 444.
[88] P.E. Sues, A.J. Lough, R.H. Morris, Inorg. Chem. 51 (2012) 9322.
[89] Z. Spichal, M. Necas, J. Pinkas, Z. Zdrahal, Polyhedron 25 (2006) 809.
[90] Z. Spichal, V. Petricek, J. Pinkas, M. Necas, Polyhedron 27 (2008) 283.
[91] E. Buckley-Dhoot, J. Fawcett, R.A. Kresinski, A.W.G. Platt, Polyhedron 28 (2009) 1497.
[92] Z. Spichal, B. Hegrova, Z. Moravec, J. Pinkas, M. Necas, Polyhedron 30 (2011) 1620.
[93] Y.-C. Tan, X.-M. Gan, J.L. Stanchfield, E.N. Duessler, R.T. Paine, Inorg. Chem. 40 (2001) 2910.
[94] A.G. Mateeva, A.S. Peregudov, E.I. Matrosov, Z.A. Starikova, S.V. Mateeva, E.E. Nifant'ev, Inorg. Chim. Acta 362 (2009) 3607.
[95] B.W. McCann, N. De Silva, T.L. Windus, M.S. Gordon, B.A. Moyer, V.S. Bryantsev, B.P. Hay, Inorg. Chem. 55 (2016) 5787.
[96] X.-M. Gan, E.N. Duessler, R.T. Paine, Inorg. Chem. 40 (2001) 4420.
[97] K.L. Nash, C. Lavallette, M. Borkowski, R.T. Paine, X. Gan, Inorg. Chem. 41 (2002) 5849.
[98] X. Gan, B.M. Rapko, E.N. Duessler, I. Binyamin, R.T. Paine, B.P. Hay, Polyhedron 24 (2005) 469.
[99] S. Pailloux, C.E. Shirima, A.D. Ray, E.N. Duessler, R.T. Paine, J.R. Klaehn, M.E. McLlwain, B.P. Hay, Inorg. Chem. 48 (2009) 3104.
[100] X.-M. Gan, S. Parveen, W.L. Smith, E.N. Duessler, R.T. Paine, Inorg. Chem. 39 (2000) 4591.
[101] D. Rosario-Amorin, S. Qizem, D.A. Dickie, Y. Wen, R.T. Paine, J. Gao, J.K. Grey, A. de Bettencourt-Dias, B.P. Hay, L.H. Delmau, Inorg. Chem. 52 (2013) 3063.
[102] S. Qizem, D. Rosario-Amorin, D.A. Dickie, R.E. Cramer, C.F. Campana, B.P. Hay, J. Podair, L.H. Delmau, R.T. Paine, Polyhedron 97 (2015) 20.
[103] D. Rosario-Amorin, E.N. Duessler, R.T. Paine, B.P. Hay, L.H. Delmau, S.D. Reilly, A.J. Gaunt, B.L. Scott, Inorg. Chem. 51 (2012) 6667.
[104] D. Rosario-Amorin, S. Qizem, D.A. Dickie, R.T. Paine, R.E. Cramer, B.P. Hay, J. Podair, L.H. Delmau, Inorg. Chem. 53 (2014) 5698.
[105] D. Rosario-Amorin, S. Qizem, D.A. Dickie, B.P. Hay, J. Podair, L.H. Delmau, R.T. Paine, Polyhedron 102 (2015) 103.
[106] T. Yaita, H. Narita, S. Suzuki, S. Tachimori, H. Shiwaku, H. Motohashi, J. Alloys Compd. 271–273 (1998) 184.
[107] J. Fawcett, A.W.G. Platt, S. Vickers, M.D. Ward, Polyhedron 23 (2004) 2561.
[108] K. Nakamura, Y. Hasegawa, H. Kawai, N. Yasuda, Y. Wada, S. Yanagida, J. Alloys Compd. 408–412 (2006) 771.
[109] Y. Hirai, T. Nakanishi, Y. Hasegawa, J. Lumin. 170 (2016) 801.
[110] K. Miyata, T. Ohba, A. Kobayashi, M. Kata, T. Nakanishi, F. Fushimi, Y. Hasegawa, ChemPlusChem 77 (2012) 277.
[111] Y. Hasegawa, R. Hieda, K. Miyata, T. Nakanishi, T. Kawai, Eur. J. Inorg. Chem. (2011) 4978.
[112] H.-B. Xu, P.-C. Jiao, B. Kang, J.-G. Deng, Y. Zhang, Sci. Rep. 3 (2199) (2013), http://dx.doi.org/10.1038/srep02199.
[113] K. Miyata, Y. Konno, T. Nakanishi, A. Kobayashi, M. Kato, K. Fushimi, Y. Hasegawa, Angew. Chem. Int. Ed. 52 (2013) 6413.
[114] Y. Hirai, T. Nakanishi, K. Miyata, K. Fushimi, Y. Hasegawa, Mater. Lett. 130 (2013) 91.
[115] T. Harada, Y. Hasegawa, Y. Nakano, M. Fujiki, M. Naito, T. Wada, Y. Inoue, T. Kawai, J. Alloys Compd. 488 (2009) 599.
[116] T. Harada, Y. Nakano, M. Fujiki, M. Naito, T. Kawai, Y. Hasegawa, Inorg. Chem. 48 (2009) 11242.
[117] M. Congiu, M. Alamiry, O. Moudam, S. Ciorba, P.R. Richardson, L. Maron, A.C. Jones, B.S. Richards, N. Robertson, Dalton Trans. 42 (2013) 13537.
[118] Md.A. Subhan, Y. Hasegawa, T. Suzuki, S. Kaizaki, Y. Shozo, Inorg. Chim. Acta 362 (2009) 136.
[119] V. Divya, R.O. Friere, M.L.P. Reddy, Dalton Trans. 40 (2011) 3257.
[120] D.B. Ambili Raj, S. Biju, M.L.P. Reddy, Dalton Trans. 38 (2009) 7519.
[121] B. Francis, D.B. Ambili Raj, M.L.P. Reddy, Dalton Trans. 39 (2010) 8084.
[122] D.B. Ambili Raj, B. Francis, M.L.P. Reddy, R.R. Butorac, V.M. Lynch, A.H. Cowley, Inorg. Chem. 49 (2010) 9055.
[123] S. Biju, M.L.P. Reddy, A.H. Cowley, K.V. Vasudevan, Cryst. Growth Des. 9 (2009) 3562.
[124] H. Xu, R. Zhu, P. Zhao, W. Huang, J. Phys. Chem. 115 (2011) 15627.
[125] H. Xu, Y. Wei, B. Zhao, W. Huang, J. Rare Earths 28 (2010) 666.
[126] J. Wang, C. Han, G. Xie, Y. Wei, Q. Xue, P. Yan, Chem. Eur. J. 20 (2014) 11137.
[127] L. Huang, B.-Q. Ma, C.-H. Huang, T.C.W. Mak, G.-Q. Yao, G.-X. Xu, J. Coord. Chem. 54 (2001) 95.
[128] J. Fawcett, A.W.G. Platt, Polyhedron 22 (2003) 967.
[129] H. Morimoto, T. Yoshino, T. Yukawa, G. Lu, S. Matsungana, Angew. Chem. Int. Ed. 47 (2008) 9125.
[130] M. Correa-Ascencio, E.K. Galvan-Miranda, F. Rascon-Cruz, O. Jimenez-Sandoval, S.J. Jimenez-Sandoval, R. Cea-Olivares, V. Jancik, R.A. Toscano, V. Garcia-Montalvo, Inorg. Chem. 49 (2010) 4109.
[131] S. Mal, M. Pietraszkiewicz, O. Pietraszkiewicz, J. Coord. Chem. 68 (2015) 367.
[132] A.M.J. Lees, A.W.G. Platt, Polyhedron 24 (2005) 427.
[133] M.W. Peters, E.J. Werner, M.J. Scott, Inorg. Chem. 41 (2002) 170.
[134] M. Nogami, M. Hashimoto, Y. Sasaoka, R. Tanabe, H. Satou, Energy Procedia 71 (2015) 12.
[135] K. Miyata, Y. Hasegawa, Y. Kuramochi, T. Nakagawa, T. Yokoo, T. Kawai, Eur. J. Inorg. Chem. (2009) 4777.
[136] F.J. Sainz-Gonzalo, M. Casimiro, C. Popovici, A. Rodriguez-Dieguez, J.F. Fernandez-Sanchez, I. Fernandez, F. Lopez-Ortiz, A. Fernandez-Gutierrez, Dalton Trans. 41 (2012) 6735.
[137] B. Lambert, V. Jacques, A. Shivanyuk, S.E. Matthews, A. Tunayar, M. Baaden, G. Wipff, V. Bohmer, J.F. Desreux, Inorg. Chem. 39 (2000) 2033.
[138] M. Atanassova, V. Lachkova, N. Vassilev, S. Varbanov, I. Dukov, Polyhedron 29 (2010) 655.
[139] F. de Maria Ramirez, S. Varbanov, J.-C.G. Bunzli, R. Scopelliti, Inorg. Chim. Acta 378 (2011) 163.
[140] F. de Maria Ramirez, T. Tosheva, E. Tashev, E. Garcia-Villafana, S. Shenkov, S. Varbanov, Polyhedron 56 (2013) 123.
[141] S.R. Menon, J.A.R. Schmidt, Tetrahedron 72 (2016) 767.
[142] S.A. Ansari, P.K. Mohapatra, W. Verboom, Z. Zhang, P.D. Dau, J.K. Gibson, L. Rao, Dalton Trans. 44 (2015) 6416.
[143] Q.-L. Guo, D.-Q. Yuan, S.-L. Ma, Y.-C. Li, W.-X. Zhu, J. Mol. Struct. 752 (2005) 7.
[144] H. El Moll, D. Semeril, D. Matt, L. Charbonniere, L. Toupet, Dalton Trans. 40 (2011) 4391.
[145] F. de Maria Ramirez, S. Varbanov, C. Cecile, G. Muller, N. Fatin-Rouge, R. Scopelliti, J.-C.G. Bunzli, J. Chem. Soc. Dalton Trans. (2002) 4505.
[146] N. Quali, J.-P. Rivera, D. Chapon, P. Delangle, C. Piguet, Inorg. Chem. 43 (2004) 1517.
[147] C.F.G.C. Geraldes, S. Zhang, A.D. Sherry, Inorg. Chim. Acta 357 (2004) 381.
[148] M.B. Husrthouse, W. Levason, R. Ratnani, G. Reid, H. Stainer, M. Webster, Polyhedron 24 (2005) 121.