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Systematics and Surprises in Lanthanide Coordination Chemistry

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In memory of Don Bradley and Allan White; mentors, encouragers, friends.

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1. Introduction

Alfred Werner was awarded the 1913 Nobel Prize in Chemistry. One of the cornerstones of his coordination theory was that the most characteristic coordination number of transition metals - such as cobalt (III) and platinum (IV) - in their complexes was six.

At that time, the chemistry of the lanthanides was in a confused state, as it was not known how many lanthanides there were; not until 1947 would promethium be fully characterised [1-3]. Even less was known about lanthanide coordination chemistry and until the 1960s it was generally assumed that lanthanide complexes were also six coordinate.

In fact, studies reported in 1937-1939 on the structures of the hydrated ethylsulfates $[Ln(H_2O)_9]$ $(EtSO_4)_3$ (Ln = Y, La, Ce, Pr, Nd, Sm, Gd, Dy) [4] and of hydrated neodymium bromate, $[Nd(H_2O)_9]$ $(BrO_3)_3$ [5] showed the presence of a tricapped trigonal prismatic 9-coordination. This was not reflected in the textbooks of the time. Thus Sidgwick refers to these structures but does not indicate the complex ions present, whilst Emeléus and Anderson devote 100 pages to transition metal coordination chemistry, but lanthanides do not feature [6, 7].

It was not until the 1960s that the picture began to change. Thus in 1963 the report of 12-coordination in the $[Ce(NO_3)_6]^{3-}$ units in $Ce_2Mg_3(NO_3)_{12}$. $24H_2O$ appeared [8] whilst in 1965 it was shown that K La(EDTA). $8H_2O$ contained nine-coordinate $[La(EDTA)(OH_2)_3]^-$ ions [9]. Subsequently it was shown that using the bulky bis(trimethylsilyl)amide ligand, three coordinate $[Ln\{N(SiMe_3)_2)_3]$ (Ln = Y, La, Ce, Pr, Nd, Sm, Eu,Gd, Ho, Yb, and Lu) could be obtained [10] whilst use of a hindered aryl group gave four coordination in $[Li(thf)_4]$ $[Ln(2,6\text{-dimethylphenyl})_4]$ (Ln = Yb, Lu) [11]. Two coordination was more recently achieved, again by using a very bulky ligand, in $[Yb\{C(SiMe_3)_3\}_2]$ [12-13].

The present situation is accurately described by Raymond et al: - 'The coordination chemistry of the lanthanides shows much structural diversity. However, there is often only a limited degree of predictability because of the absence of strong ligand field effects, resulting in small energetic differences between different geometric arrangements and/or coordination numbers.' [14]

2. The Lanthanide contraction.

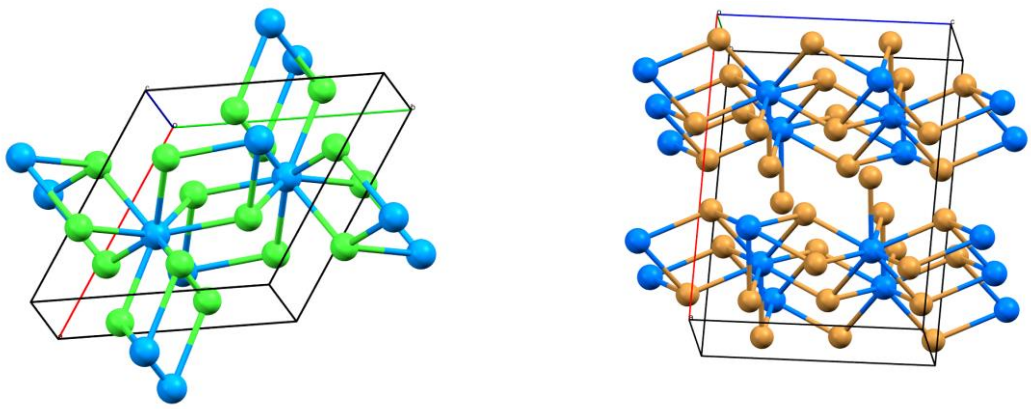
This is a key concept in lanthanide chemistry. As Atomic Number increases, there is a progressive decrease in ionic radius, with the last lanthanide being some 16 % smaller than the first. The cause of this is the increase in effective nuclear charge experienced by the outer electrons, mainly caused by the incomplete shielding of the 5s and 5p electrons by the 4f electrons, with about 10% due to relativistic effects [15-18].

The 'lanthanide contraction' manifests itself in various ways. For example, the increase in charge density with increasing Z means that in general there is an increase in the stability of complexes formed from La^{3+} to Lu^{3+} [19-20]. Because lanthanide ores contain mixtures of a number of chemically very similar metals, their separation (and the availability of high-purity compounds of individual elements) generally makes use of this.

Another effect of this is the decrease in coordination number in simple binary compounds in the solid state, in accord with what would be predicted by a simple model based on packing of spherical ions. Thus amongst the trihalides, the coordination number decreases from 11 in LaF_3 to 9 in LuF_3; from 9 in $LaCl_3$ and $LaBr_3$ to 6 in $LuCl_3$ and $LuBr_3$; and from 8 in LaI_3 to 6 in LuI_3 [21].

It is possible to envisage a species with a ML_9 coordination sphere (L = a monodentate donor such as a halide or water), this having a D_{3h} tricapped trigonal prismatic structure like the classic lanthanide aqua ion structure. As the radius of the central metal decreases, the non-bonding inter-ligand repulsions will become greater, to the point where one ligand is squeezed out forming a species with an eight coordinate geometry, in other words changing from the UCl_3 to the $PuBr_3$ structure type (Fig. 1). This of course represents the difference between the 9 coordinate aqua ions formed by the early lanthanides (La to Eu) and the 8 coordinate aqua ions formed by the later lanthanides (Dy to Lu) [22].

When ligands involved have a greater denticity than one, it is possible that this strain may be removed in other ways, one possibility being to introduce asymmetry in the bidentate coordination of a group like nitrate.



(a) (b)

Fig. 1. (a) The structure of UCl_3 showing the 9-coordinate U atoms. (b) The structure of PuBr3 showing the 8-coordinate Pu atoms.

Solid state effects are influential, thus crystals of the hydrated lanthanide ethylsulfates, bromates and triflates contain nine-coordinate $[Ln(H_2O)_9]^{3+}$ ions (Fig. 2) across the whole series [23-25] whilst for the later lanthanides the $[Ln(H_2O)_8]^{3+}$ ion predominates in aqueous solution.

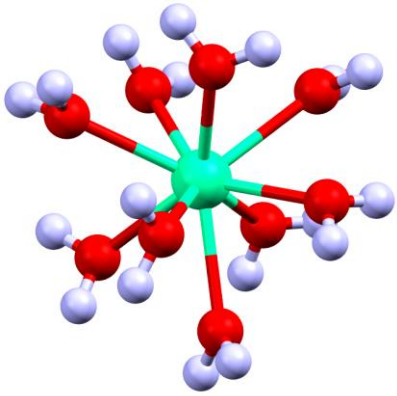


Fig. 2. The structure of the cation $[Ho(H_2O)_9]^{3+}$ [26] showing the 9-coordinate geometry

Fig. 3 shows how bond lengths in the $[Ln(H_2O)_9]^{3+}$ ions present in the ethylsulfate salts show the expected smooth contraction with increasing atomic number

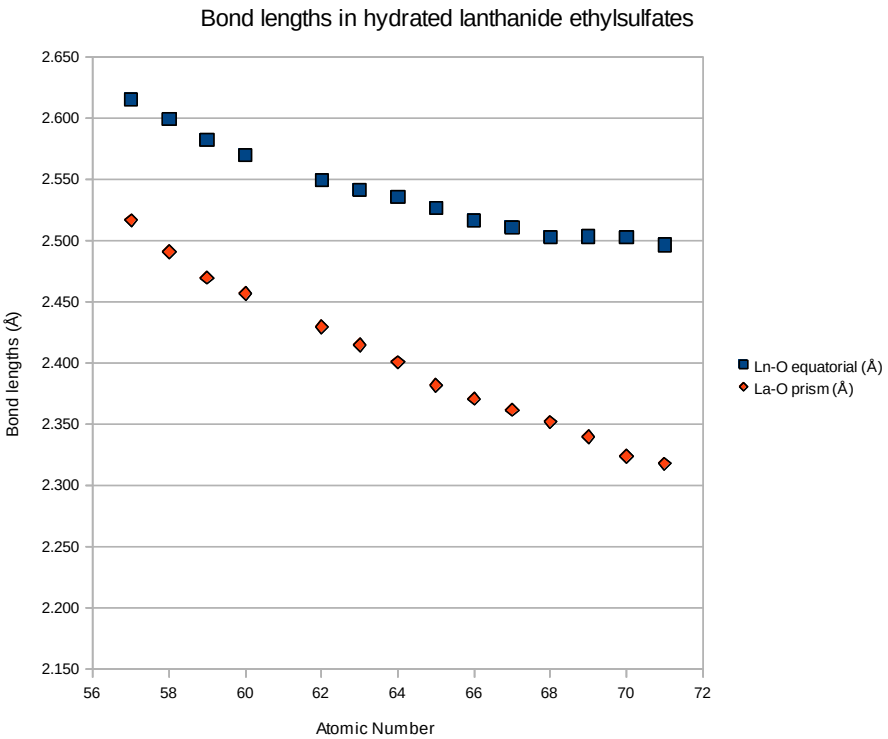


Fig. 3. The lanthanide contraction across the lanthanide series illustrated by the decrease in Ln-O bond lengths in the $[Ln(H_2O)_9]^{3+}$ series. The Ln-O distances are averaged over the sets of equivalent bonds in the structures with the error on individual points in the graph being of the order of ±0.005 Å.

Relatively few systematic studies have been made of the effect of the variation of ionic radius upon the stoichiometry and geometry of lanthanide complexes with other ligands. Thus often an investigation might study the structure of the complexes formed by a ligand with one early lanthanide, one in mid-series, and one of the later metals. Recent exceptions involving the determinations of the structures of a whole series include the neopentoxides, which all have the tetrameric structure $[Ln(\mu\text{–}ONep)_2(ONep)]_4$ (Ln = Sc, Y, La-Lu except Pm; Neop = CH_2CMe_3) [27] Another complete family to be characterised for all the lanthanides except promethium is $[Ln(L)(H_2O)]$ (L = TREN-1,2-HOIQO, a hexadentate O_6-donor ligand) [14]

We have therefore investigated of a few families of simple lanthanide complexes in order to study how the decrease in ionic radius of the Ln^{3+} ion by some 16% across the series affects the stoichiometry and structures of the complexes obtained.

3. Complexes of lanthanide nitrates with 2, 2'-bipyridyl (bipy)

Complexes $[Ln(bipy)_2(NO_3)_3]$ were first prepared by three groups of workers in the 1960s [28-30]. These form an isomorphous and isostructural series, with the first structure in the series, the terbium complex, being reported in 1969 [31]; the structure determination was carried out by single crystal crystallography using Weissenberg photographic techniques. Then the structures of the extreme members of the series reported in 1972 (La) [32] and 1996 (Lu) [33]. Subsequently, the structures of the complexes of the intermediate elements except for those of Pm, Ho and Yb have been determined crystallographically (Pr [34]; Nd [35]; Sm [36]; Eu [37]; Dy [38]; Er [39]). Since the structures have been determined over several decades, we have determined some of the missing structures in the series, together with redeterminations of several of the structures, all at the same temperature of 150 K, to provide a consistent series. These structures have been deposited directly with the Cambridge Crystallographic Data Centre (La, CCDC No. 1525425; Ce, CCDC No. 1492899; Pr, CCDC No. 1521708; Nd, CCDC No. 1521896; Gd, CCDC No. 1525411; Tm, CCDC No. 1523918; Lu, CCDC No. 1525632). The molecular structure of the Eu complex [37] which illustrates the 10-coordinate geometry throughout the series is shown in Fig. 4.

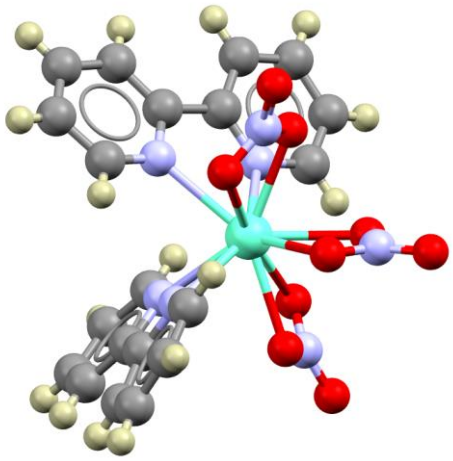


Fig. 4. The structure of the 10-coordinate $[Eu(bipy)_2(NO_3)_3]$ complex [34]

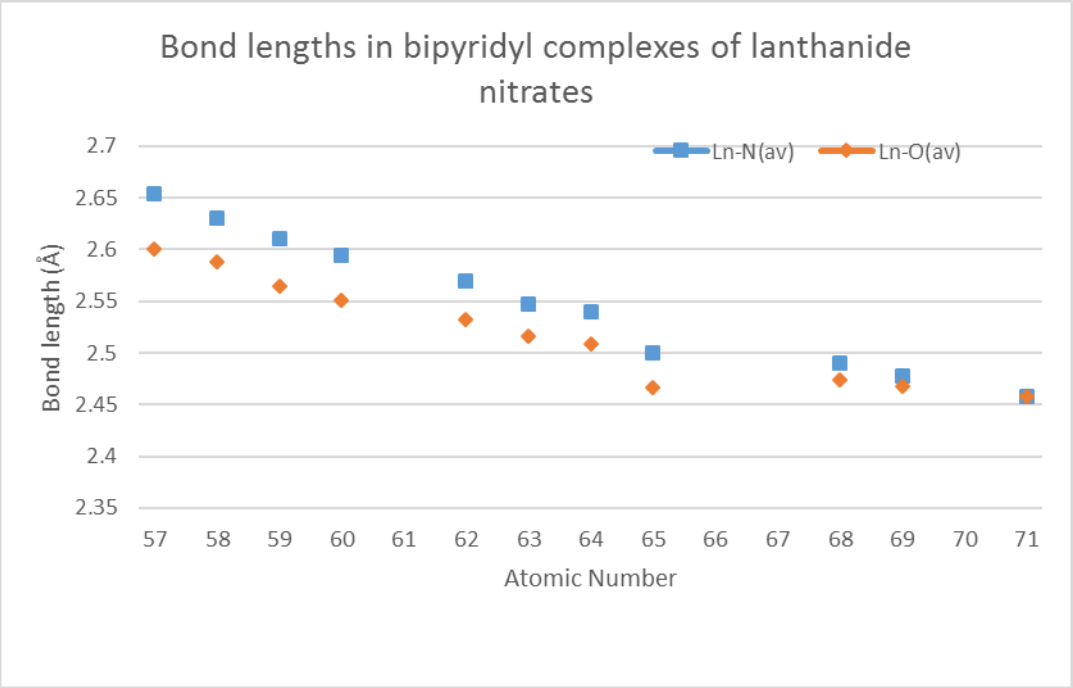


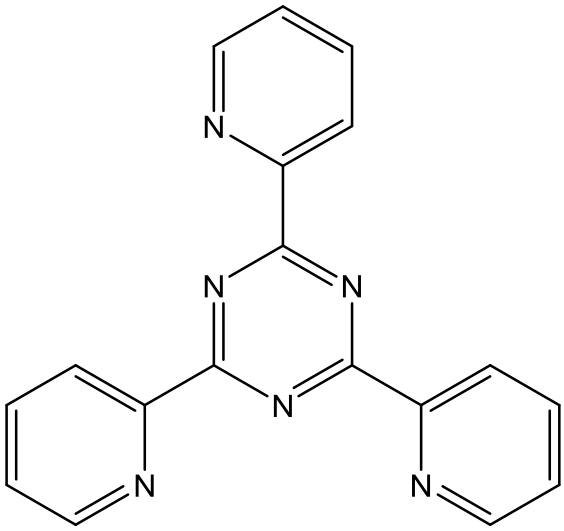
Fig. 5. The average Ln-N and Ln-O bond lengths in the structurally determined members of the series $[Ln(bipy)_2(NO_3)_3]$ where the Ln ion is 10-coordinate right across the series. The majority of the complexes have had their structures determined at 150 K, and where available data directly deposited into the CCDC has been used. The Ln-O and Ln-N bond lengths quoted are averaged over all the unique Ln-O and Ln-N distances in each structure, and the error bar on each point on the graph is of the order of ±0.005 Å.

As shown in Fig. 5, bond lengths show a smooth decrease with increasing atomic number at the beginning of this isostructural family. The entry for $[Tb(bipy)_2(NO_3)_3]$ [31] (element with atomic number 65 in Fig. 5) shows the greatest deviation from this trend, but this is the structure that was determined at room temperature using Weissenberg photography as the data collection method, and the errors associated with it are an order of magnitude larger

than for the other members of the series. Hence, this structure might be expected to fit less well than the others. In the last three members of the series, $[Ln(bipy)_2(NO_3)_3]$ (Ln = Er, Tm, Lu), the difference between the average Ln-N and Ln-O decreases so that by Lu the Lu-N and Lu-O average distances are very similar. This may be a reflection of the smaller size of the metal ion, and the requirement to pack 10 coordinating atoms around it.

Along the series the coordination of the two bridgehead N-atoms in the two bipyridyl ligands remains pretty symmetrical, however, the two Ln-O distances for the crystallographic independent nitrate groups show increasing asymmetry across the series (for the other nitrate group the two Ln-O distances are related by crystallographic symmetry and thus are equal). To illustrate this point, for the La complex the two La-O distances are 2.626(3) and 2.593(3) Å, while for Eu they are 2.561(3) and 2.495(3) Å, and for Lu they are 2.550(3) and 2.408(3) Å, respectively. Thus, the differences increase from 0.033 Å, to 0.066 Å, and to 0.142 Å, for La, Eu and Lu, respectively. The increase in asymmetry may be associated with the increased steric interaction between the ligands as they pack around a smaller metal ion.

4. Complexes of the lanthanide nitrates with 2, 4, 6-tri-α-pyridyl-1,3,5-triazine (tptz)



These compounds were originally reported in 1969 as $[Ln(tptz)(NO_3)_3(H_2O)]$ (Ln = Y, La-Lu except Pm), the syntheses being carried out in ethanol [40].

We found that reaction between $Ln(NO_3)_3.xH_2O$ and the ligand in ethanol give isomorphous crystalline complexes $[Ln(tptz)(NO_3)_3(H_2O)].2C_2H_5OH$ (Ln = Y , La-Yb except Pm) for all these elements except the smallest, lutetium. All contain three bidentate nitrate groups as well as a coordinated water molecule, the lanthanides being 10-coordinate. 2, 4, 6-tri-α-pyridyl-1,3,5-triazine (tptz) acts as a chelating terdentate ligand, like 2, 2'; 6', 2"-terpyridine (terpy), in all the complexes we isolated [41].

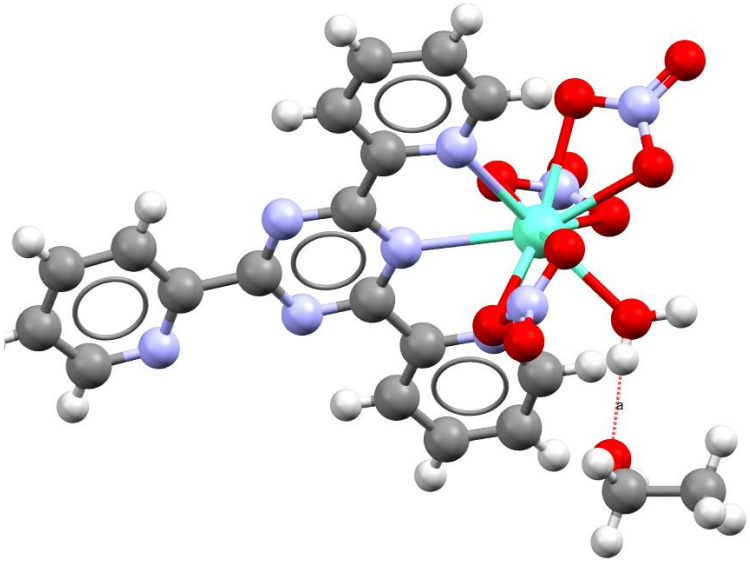


Fig. 6. The structure of $[Eu(tptz)(NO_3)_3(H_2O)].\ 2C_2H_5OH$ as an exemplar of the series $[Ln(tptz)(NO_3)_3(H_2O)].2C_2H_5OH$. A hydrogen bonded ethanol molecule is included to illustrate the importance of the solvent in the crystallisation process.

Our syntheses using ethanol as solvent readily afforded crystals $[Ln(tptz)(NO_3)_3(H_2O)].2C_2H_5OH$ that proved suitable for X-ray diffraction (Fig. 6). Others carried out the syntheses in MeCN, finding it 'very difficult to grow crystals and very few structures have been obtained' [42]; in fact they have reported the structure of just $[Sm(tptz)(NO_3)_3(H_2O)].2H_2O$ [43]. Thus uncoordinated solvent molecules trapped in the lattice can influence crystal growth.

In the case of ytterbium, crystals of a second complex, $[Yb(tptz)(NO_3)_3(C_2H_5OH)]$, were obtained from the reaction mixture, along with $[Yb(tptz)(NO_3)_3(H_2O)].2C_2H_5OH$. This complex contains 9-coordinate ytterbium, one nitrate being monodentate, and an ethanol molecule also being coordinated. The corresponding lutetium complex, $[Lu(tptz)(NO_3)_3(C_2H_5OH)]$, resulted from the reaction between lutetium nitrate and tptz in ethanol; carrying out this synthesis in other solvents like CH_3CN and CH_3OH afforded $[Lu(tptz)(NO_3)_3(H_2O)].\ CH_3CN$ (Fig. 7) or $[Lu(tptz)(NO_3)_2(H_2O)_2]NO_3.\ 3\ CH_3OH$ respectively, both of these also containing 9-coordinate lutetium. The earlier metals appear to form the same complex species, $[Ln(tptz)(NO_3)_3(H_2O)]$, if the syntheses are carried out in CH_3CN, but reaction of hydrated lanthanum nitrate with tptz in methanol yields 11-coordinate $[La(tptz)(NO_3)_3(CH_3OH)_2]$.

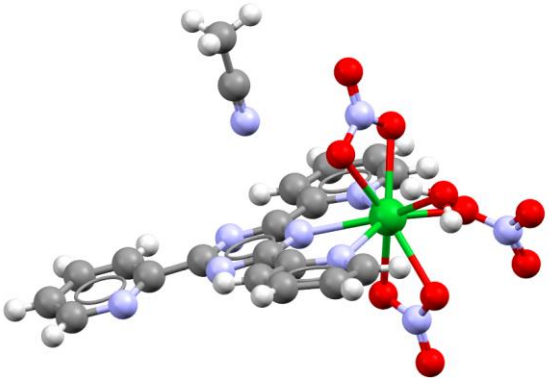


Fig. 7. The structure of the 9-coordinate $[Lu(tptz)(NO_3)_3(H_2O)]$. CH_3CN. The structure shown includes the uncoordinated MeCN solvent molecule.

Examination of the family of isostructural 10-coordinate compounds $[Ln(tptz)(NO_3)_3(H_2O)]$.2 EtOH reveals a steady decrease in bond length with increasing Z (and decreasing ionic radius), of the lanthanide ion. First - comparing the extreme members of the series, the lanthanum and ytterbium compounds, the average Ln–N distances are 2.687 Å (La) and 2.514 Å (Yb); the average Ln–O (nitrate) distances are 2.606 Å (La) and 2.457 Å (Yb); and the Ln–O (water) distances are 2.452 Å (La) and 2.270 Å (Yb). So the changes in average bond length range from 0.149 Å (Ln–O (nitrate)) to 0.182 Å (Ln–O (water)), roughly what would be expected on the basis of ionic radii. Fig. 8 makes these trends clear.

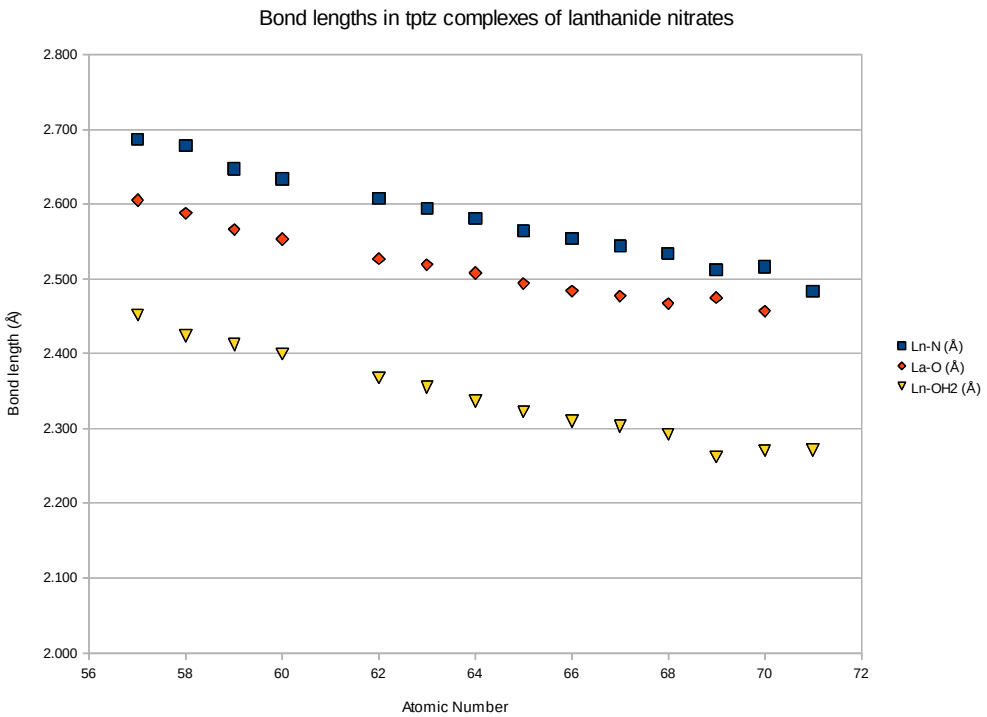


Fig. 8. Ln-N, Ln-O and Ln-OH_2 bond lengths in the series $[Ln(tptz)(NO_3)_3(H_2O)]$.2 EtOH. The error bar on each point on the graph is of the order of ±0.005 Å.

Obviously as the ionic radius of the lanthanide decreases, so there are tighter non-bonding contacts between the coordinated ligands, and we wondered how this manifested itself. An obvious point to examine was the binding of the nitrate groups – how regular was their coordination distance?

Starting with the lanthanum compound $[La(tptz)(NO_3)_3(H_2O)]$. $2C_2H_5OH$, the La–O (nitrate) distances range from 2.570(1) to 2.631(1) Å, a spread of values of 0.061 Å. As Z increased, this range increased quite steadily - 0.069 Å (Ce); 0.070 Å (Pr); 0.078 Å (Nd); 0.085 Å (Sm); 0.093 Å (Eu); 0.099 Å (Gd); 0.113 Å (Tb); 0.119 Å (Dy); 0.128 Å (Ho); 0.143 Å (Er); 0.138 Å (Tm); then quite abruptly increasing to 0.180 Å in $[Yb(tptz)(NO_3)_3(H_2O)]$.$2C_2H_5OH$. It was not possible to isolate a lutetium analogue, nine coordinate $[Lu(tptz)(NO_3)_3(C_2H_5OH)]$ being the reaction product, thereby confirming the view of increasing congestion.

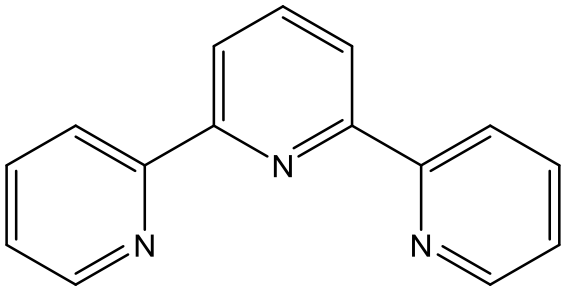
Within individual nitrate groups, the picture is also one of increased asymmetry in coordination as Z increases. Thus in $[La(tptz)(NO_3)_3(H_2O)]$. $2C_2H_5OH$, the difference in the La-O distance between the coordinated oxygens in each bound nitrate were 0.036, 0.047 and 0.053 Å; for $[Yb(tptz)(NO_3)_3(H_2O)]$. $2C_2H_5OH$ these distances were 0.069, 0.127 and 0.168 Å. This mimics the trend previously discussed for the $[Ln(bipy)_2(NO_3)_3]$ series discussed in Section 3.

Although we did not isolate 11-coordinate complex $[La(tptz)(NO_3)_3(H_2O)_2]$ (for which the corresponding terpy complex exists; which will be discussed in Section 5), the corresponding methanol complex $[La(tptz)(NO_3)_3(CH_3OH)_2]$ could be obtained. Moreover, in another study of complexes of the closely related 4-amino-bis(2,6-(2-pyridyl))1,3,5-triazine ligand (abptz), both ten co-ordinate $[La(abptz)(NO_3)_3(H_2O)]$ and eleven co-ordinate $[La(abptz)(NO_3)_3(H_2O)_2]$ were isolated from the same reaction mixture [41]. Bond lengths are, as expected, longer in $[La(tptz)(NO_3)_3(CH_3OH)_2]$ than in the 10-coordinate $[La(tptz)(NO_3)_3(H_2O)]$, by some 0.07 Å (La-N) and 0.03 Å (La-O(nitrate)). Presumably the 11-coordinate $[La(tptz)(NO_3)_3(H_2O)_2]$ exists in solution but is not isolated for reasons of solubility.

As already noted, the choice of solvent for the synthesis of the lutetium complex is highly influential, with $[Lu(tptz)(NO_3)_3(C_2H_5OH)]$, $[Lu(tptz)(NO_3)_3(H_2O)]$. CH_3CN or $[Lu(tptz)(NO_3)_2(H_2O)_2]NO_3$. 3 CH_3OH isolated, all containing 9-coordinate lutetium. In two of these, one nitrate group is monodentate, and in the ethanol complex a coordinated water molecule is present, although this is not further linked to the uncoordinated nitrate oxygen as observed in the similar terpy complexes to be discussed in Section 5.

Studying this series indicates both the value of studying the whole series of elements - as the atypical behaviour is here shown right at its end - as well as that of examining the role that solvent can have [41].

5. Complexes of lanthanide nitrates with 2, 2'; 6', 2"-terpyridine (terpy)



Reaction of hydrated lanthanide nitrates with 1 mole of terpy in MeCN solution gives complexes $[Ln(terpy)(NO_3)_3(H_2O)_n]$ (Ln = La, n = 2; Ln = Ce – Dy except Pm, n = 1; Ln = Ho-Lu, n = 0). The smallest lanthanides form 9-coordinate complexes, whilst the lanthanum complex is 11-coordinate, with lanthanum bound to two water molecules, and the majority of the metals form 10-coordinate complexes in which just one water molecule is also bound to the lanthanide. All feature bidentate nitrate groups [37, 44, 45].

Others have isolated $[M(NO_3)_3(terpy)(H_2O)]$.terpy (M = Y, Ho, Er, Tm and Yb), in which a second terpy molecule is not coordinated to the metal [46, 47]. We also obtained the yttrium complex, formed even when a 1:1 metal to ligand ratio is used. Synthesised by another group, $[Tm(NO_3)_3(terpy)(H_2O)]$ contains 9-coordinate thulium, bonded to a terdentate terpy, two bidentate nitrates, one unidentate nitrate and a water molecule [47].

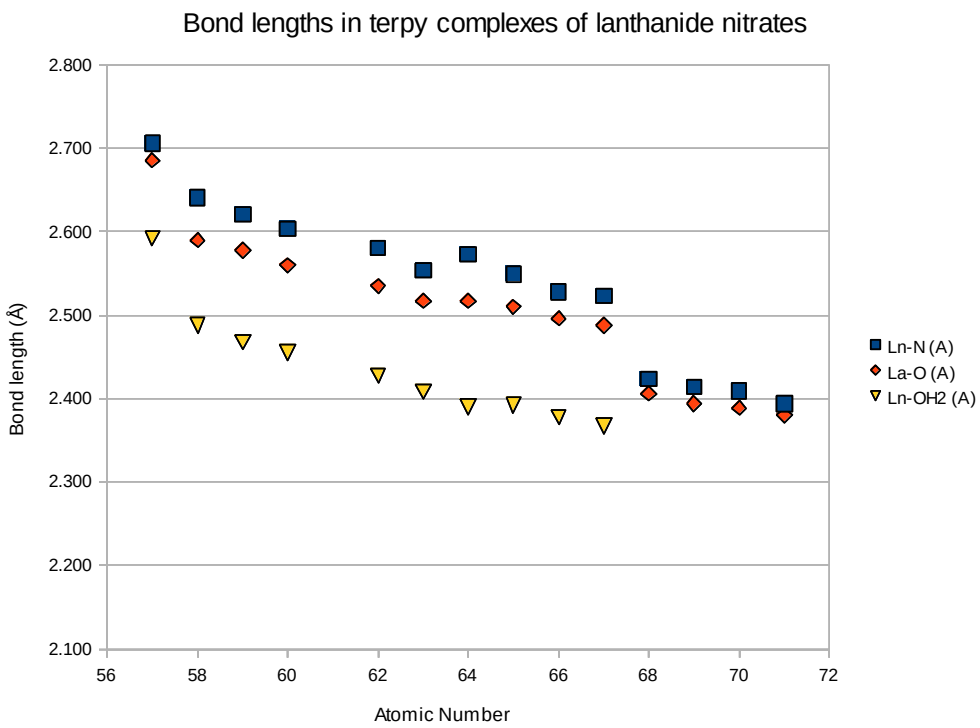


Fig. 9. Ln-N, Ln-O and Ln-OH_2 bond lengths in the series [Ln(terpy)$(NO_3)_3(H_2O)_n$]. The error bar on each point on the graph is of the order of ±0.005 Å.

Table 1Average bond lengths in the complexes Ln(terpy)$(NO_3)_3(H_2O)_x$

	Ionic Radius / Å	M-N / Å	M-O (NO_3) / Å	M-O (H_2O) / Å	x
La	1.216	2.706	2.686	2.599	2
Ce	1.196	2.641	2.590	2.488(1)	1
Pr	1.179	2.621	2.578	2.468(3)	1
Nd	1.163	2.604	2.560	2.449(3)	1
Sm	1.132	2.581	2.535	2.428(2)	1
Eu	1.120	2.554	2.517	2.408(4)	1
Gd	1.107	2.573	2.517	2.390(4)	1
Tb	1.095	2.549	2.510	2.392(4)	1
Y	1.075	2.521	2.488	2.330(4)	1
Dy	1.083	2.528	2.496	2.378(3)	1
Ho	1.072	2.523	2.488	2.367(3)	1
Er	1.062	2.424	2.406		0
Tm	1.052	2.414	2.394		0
Yb	1.042	2.409	2.389		0
Lu	1.032	2.394	2.380		0

For the family [Ln(terpy)$(NO_3)_3(H_2O)_n$] the trends in the Ln-N, Ln-O and Ln-OH_2 are illustrated in Fig. 9, while the bond parameters themselves are presented in Table 1. There is a smooth variation with increasing atomic number (and decreasing ionic radius) of the lanthanide, with discontinuities at the point of coordination number change.

Although this family contains only one 11-coordinate compound, [La(terpy)$(NO_3)_3(H_2O)_2$] (Fig. 10), its bond lengths are closely comparable to those of [La(terpy)$(NO_3)_3(MeOH)_2$], prepared by others [48].

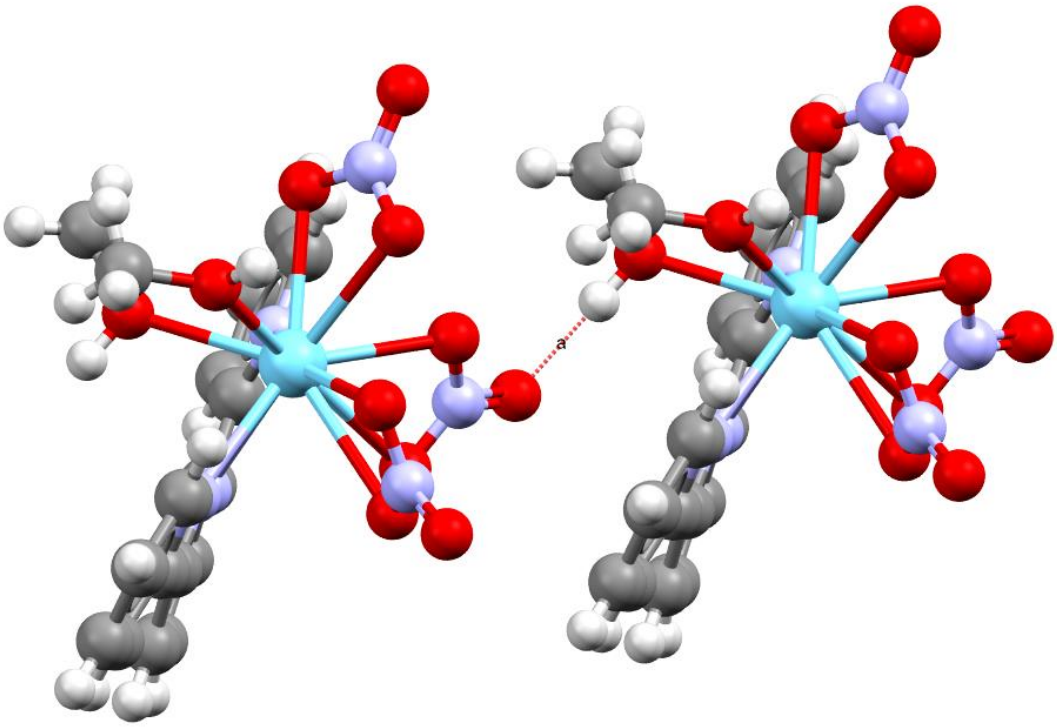


Fig. 10. The structure of [La(terpy)$(NO_3)_3(H_2O)_2$] showing the two crystallographically independent molecules in the asymmetric unit linked by a hydrogen bond.

Again, although we did not isolate a similar 11-coordinate [Ce(terpy)$(NO_3)_3(H_2O)_2$], others have isolated eleven co-ordinated Ce(terpy)$(NO_3)_3(MeOH)_2$ [49]. Significantly, in both the 11-coordinate lanthanum compounds one out of the six metal-oxygen distances involving the nitrate groups is significantly longer than the others. Thus, in [La(terpy)$(NO_3)_3(MeOH)_2$], five La-O distances fall in the range 2.596 – 2.727 Å, whereas the sixth one is 2.926(3) Å; in [La(terpy)$(NO_3)_3(H_2O)_2$], where there are two different molecules in the asymmetric unit of the unit cell, the ten La-O (nitrate) distances range from 2.617 to 2.705 Å, with the other two oxygens being 2.794 and 2.846 Å away. A similar phenomenon is observed in [Ce(terpy)$(NO_3)_3(MeOH)_2$]. The Ce-O distances to five of the oxygen atoms of the nitrate

groups vary from 2.537 to 2.712 Å, whereas the distance for the sixth oxygen is 2.942 Å. This evidently reflects congestion in the coordination sphere, relieved by the displacement of one oxygen atom slightly away from lanthanum. It is interesting that this route is chosen rather than the alternative of just one solvent molecule binding to the metal.

As already noted, in the study of complexes of 4-amino-bis(2,6-(2-pyridyl))1,3,5-triazine (abptz), both ten co-ordinated La(abptz)$(NO_3)_3(H_2O)_2$ and eleven co-ordinated La(abptz)$(NO_3)_3(H_2O)_2$ were isolated from the same reaction mixture, indicating that both complexes were present and that they were of comparable solubility [42].

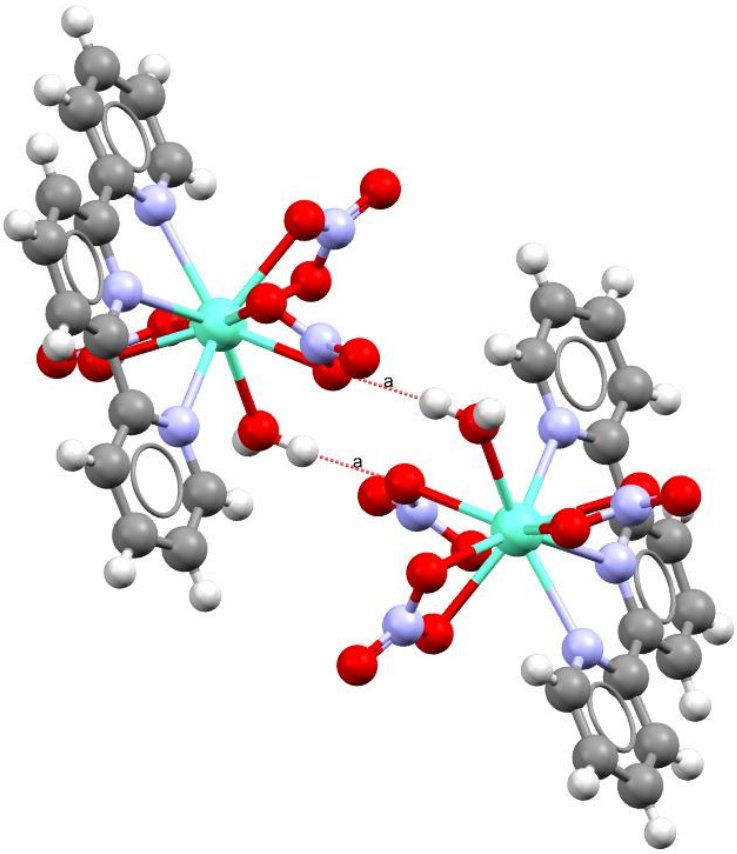


Fig. 11. The structure of 10-coordinate [Eu(terpy)$(NO_3)_3(H_2O)$] complex. Within the crystal structure there are two crystallographically independent molecules linked by hydrogen bonds between the coordinate water molecules and a nitrate oxygen in the adjacent molecule.

The majority of the complexes isolated were 10-coordinate [Ln(terpy)$(NO_3)_3(H_2O)$] (Ln = Ce-Ho) (Fig. 11) . Their structures show a smooth transition in bond lengths, closely comparable to the 0.13 Å change expected on the basis of the difference of the ionic radii for 10 co-ordinate Ce^{3+} and Ho^{3+} [50]. For individual compounds, bond lengths compare closely with those of the 10 coordinate tptyz and bipy analogues. Thus the respective Ho-N and Ho-O distances of 2.544 and 2.477 Å in [Ho(tptz)$(NO_3)_3(H_2O)$] [41] compare closely with the values

of 2.523 Å for Ho-N and 2.488 Å for Ho-O in [Ho(terpy)(NO_3)$_3$(H_2O)]. Similarly in [Pr(terpy)(NO_3)$_3$(H_2O)], average Pr-N and Pr-O distances are 2.621 and 2.577 Å respectively, compared with the corresponding values of 2.625 and 2.570 Å in [Pr(bipy)$_2$(NO_3)$_3$].

For the smaller lanthanides after holmium, no hydrated complexes are isolated, with nine coordinate Ln(terpy)(NO_3)$_3$ (Ln = Er-Lu) (Fig. 12) being the products, again containing three bidentate nitrate groups. Once more there is a smooth trend of decreasing bond length with decreasing ionic radius.

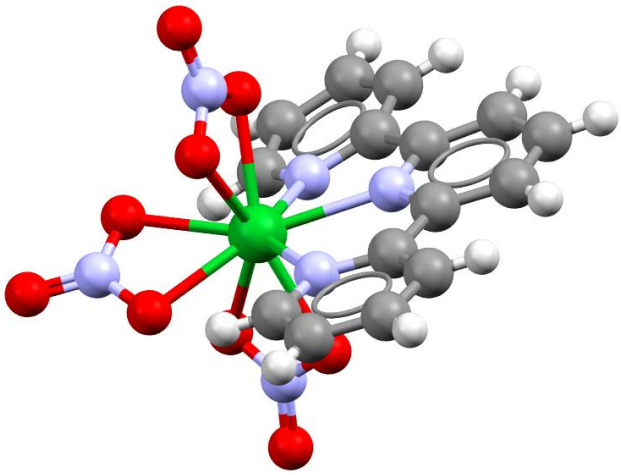


Fig. 12. The molecular structure of [Lu(terpy)(NO_3)$_3$]. With no coordinated donor solvent molecules there are no hydrogen bonds to adjacent molecules in the crystal unlike in the structure of [Eu(terpy)(NO_3)$_3$(H_2O)]

Comparing the structures of the "extreme" lanthanide compounds, Er(terpy)(NO_3)$_3$ and Lu(terpy)(NO_3)$_3$, the average Ln-N bond length decreases from 2.424 Å in the erbium compound to 2.394 Å in the lutetium compound, corresponding changes in Ln-O (nitrate) being from 2.406 Å to 2.380 Å. However, this latter change masks an increasing congestion in the coordination sphere, accommodated within the coordinated nitrates. The spread of Ln-O distances in the coordinated nitrate groups increases from 0.070 Å in the erbium complex to 0.090 Å in the lutetium compound. Despite scandium being substantially smaller than yttrium and the later lanthanides, scandium forms [Sc(terpy)(NO_3)$_3$], previously characterised by others [51]. The Sc-O distances in [Sc(terpy)(NO_3)$_3$] range from 2.232(2) Å to 2.458(2) Å, a considerably bigger spread of distances (0.226 Å) than observed even in [Lu(terpy)(NO_3)$_3$], reflecting the difficulty in arranging the nine donor atoms round the small Sc^{3+} ion. Nonetheless, no strain is found within the more rigid terpy ligand; any strain is

accommodated within the metal-nitrate coordination sphere, as is also the case with the tptz complexes.

Solvent plays a significant role in the complex isolated from the reaction between terpy and the hydrated lanthanide nitrates. Whilst earlier lanthanides give the same products in their reaction with terpy in either MeCN or ethanol, later lanthanides afford [Ln(terpy)$(NO_3)_3$(EtOH)] (Ln = Dy-Lu, Y) (Fig. 13) from reaction in ethanol [43, 45, 52]. In these compounds, the metal ion is 9-coordinated with a tridentate terpyridyl, two bidentate nitrate groups, one monodentate nitrate group, and a coordinated ethanol. The un-coordinated oxygen of the monodentate nitrate group is over 1.2 Å further from the lanthanide than are the coordinated oxygen atoms. The relevant bond parameters for this short series of structures are presented in Table 2.

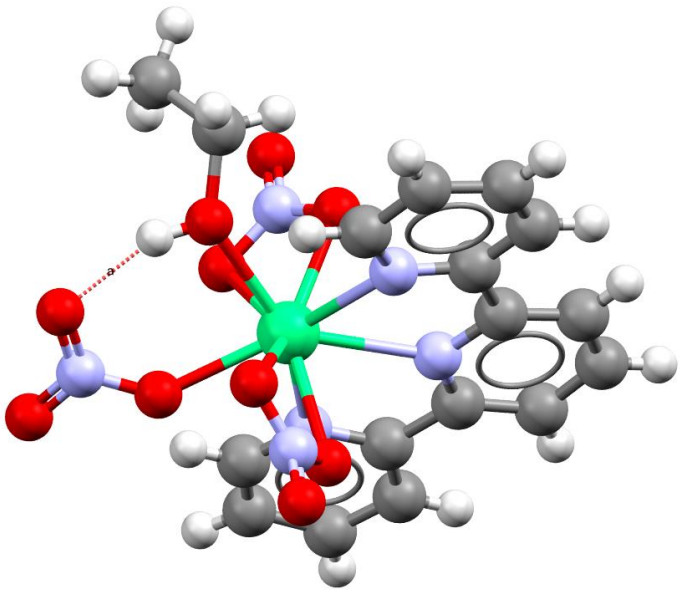


Fig. 13. The structure of [Er(terpy)$(NO_3)_3$(EtOH)] showing the intramolecular hydrogen bond between the monodentate nitrate and the coordinated ethanol molecule.

Table 2 Bond length of the complexes Ln(terpy)$(NO_3)_3$(EtOH)

	M-N / Å	Av. M-N / Å	M-O (NO_3) / Å	Av. M-O (η^2) / Å	M-O (η^1) / Å	M-OHEt / Å
Dy	2.499(8)	2.503	2.403(7)	2.442	2.309(8)	2.340(7)
	2.500(8)		2.413(7)			
	2.509(8)		2.466(8)			
			2.485(8)			
Ho	2.484(9)	2.485	2.396(8)	2.445	2.281(9)	2.342(8)
	2.484(8)		2.421(8)			
	2.486(9)		2.472(10)			

			2.489(9)			
Er	2.467(3)	2.475	2.373(3)	2.430	2.280(3)	2.338(3)
	2.475(3)		2.405(3)			
	2.484(3)		2.450(3)			
			2.290(3)			
Tm	2.453(4)	2.461	2.358(3)	2.416	2.270(3)	2.308(4)
	2.459(4)		2.388(3)			
	2.472(4)		2.440(3)			
			2.477(3)			
Yb	2.446(4)	2.455	2.355(3)	2.415	2.261(4)	2.302(4)
	2.457(4)		2.370(3)			
	2.462(4)		2.447(4)			
			2.486(4)			
Lu	2.444(3)	2.459	2.346(3)	2.414	2.279(3)	2.297(3)
	2.455(3)		2.482(3)			
	2.477(3)		2.382(3)			
			2.444(3)			
Y	2.496(6)	2.508	2.392(6)	2.442	2.282(7)	2.339(5)
	2.498(7)		2.425(6)			
	2.530(7)		2.471(7)			
			2.479(6)			

This structure type can be thought of as being derived from a Ln(terpy)(η^2-NO_3)$_3$ structure by attack of an ethanol molecule on the metal causing the breaking of a Ln-O bond in a bidentate nitrate group. Other compounds featuring this kind of linkage involving either a water molecule or an ethanol next to the monodentate nitrate include [Lu(tptz)(NO_3)$_3$(EtOH)] [41]and [Ln(terpy)(NO_3)$_3$(H_2O)] (Ln =Tm, Y) [46, 47].

A comparison of the bond lengths for one of the 9-coordinated [Ln(terpy)(NO_3)$_3$] (Ln = Er-Lu) with the similarly 9-coordinate [Ln(terpy)(NO_3)$_3$(EtOH)] indicated that the latter are the more congested molecules. Thus in [Er(terpy)(NO_3)$_3$], average Er-N and Er-O (bidentate nitrate) distances are 2.424 Å and 2.406 Å, respectively, compared with Er-N of 2.475 Å and Er-O of 2.430 Å in [Er(terpy)(NO_3)$_3$(EtOH)]. This reflects the replacement of a bidentate ligand with a small bite angle by two monodentate ligands. This congestion increases as the lanthanide becomes smaller, and can be tracked by following the spread of Ln-O distances within the coordination sphere; this increases from 0.082 Å (Ln = Dy) to 0.136 Å (Ln = Lu). Since Sc^{3+} is smaller than even the smallest Ln^{3+} ion, we also investigated the reaction of scandium nitrate with terpy in ethanol to see whether it yielded an ethanol complex of this type, but the product was found to be the known [Sc(terpy)(NO_3)$_3$] [51].

Carrying out the synthesis in methanol leads to 11-coordinate [Ln(NO_3)$_3$(terpy)(MeOH)$_2$] (Ln = La, Ce) for the two biggest lanthanides. However, when we carried out this reaction for the

succeeding lanthanides praseodymium and neodymium, the known complexes $[Ln(NO_3)_3(terpy)(H_2O)]$ (Ln = Pr, Nd) were the products.

A further effect of solvent upon the product isolated is found [48] when reacting terpy with the lanthanide nitrate in MeCN followed by crystallisation from water; the earlier members of the lanthanide series form $[Ln(terpy)(NO_3)_2(H_2O)_3]\cdot NO_3$ (Ln = La-Gd) and the later lanthanides form $[Ln(terpy)(NO_3)_2(H_2O)_2]\cdot NO_3\cdot 2H_2O$ (Ln = Tb-Lu, Y). In these compounds, just one nitrate group has been replaced in the coordination sphere by further water molecules. This sheds light upon the variable stoichiometry of the complexes reported by Sinha in his initial survey of terpy complexes of the higher lanthanides [53]. The formulae given for compounds of successive lanthanides were $Tb(terpy)(NO_3)_3.\ 0H_2O$; $Dy(terpy)(NO_3)_3.\ 2H_2O$; $Ho(terpy)(NO_3)_3.\ 2H_2O$; $Er(terpy)(NO_3)_3.\ 3H_2O$; $Tm(terpy)(NO_3)_3.\ 1H_2O$; $Yb(terpy)(NO_3)_3.1H_2O$. The possibility of partial hydrolysis in some of these compounds is one that explains this variation.

The role of the solvent is therefore crucial. For example, it cannot be doubted that species $Pr(terpy)(NO_3)_3(ROH)$ (R = Me, Et) are present in the methanolic and ethanolic solutions which ultimately yield crystals of $Pr(terpy)(NO_3)_3(H_2O)$, which is also obtained from MeCN, so it must be assumed that it is the lower solubility of the hydrate that leads to its isolation.

A summary of the discussion is presented in Figs 14-16 which show how the solvent used affects the solution equilibrium and the complex obtained upon crystallisation. The lanthanum, dysprosium and thulium systems with the terpy ligand and the nitrate counter ions are used by way of example of the complex solution environment for these lanthanide species.

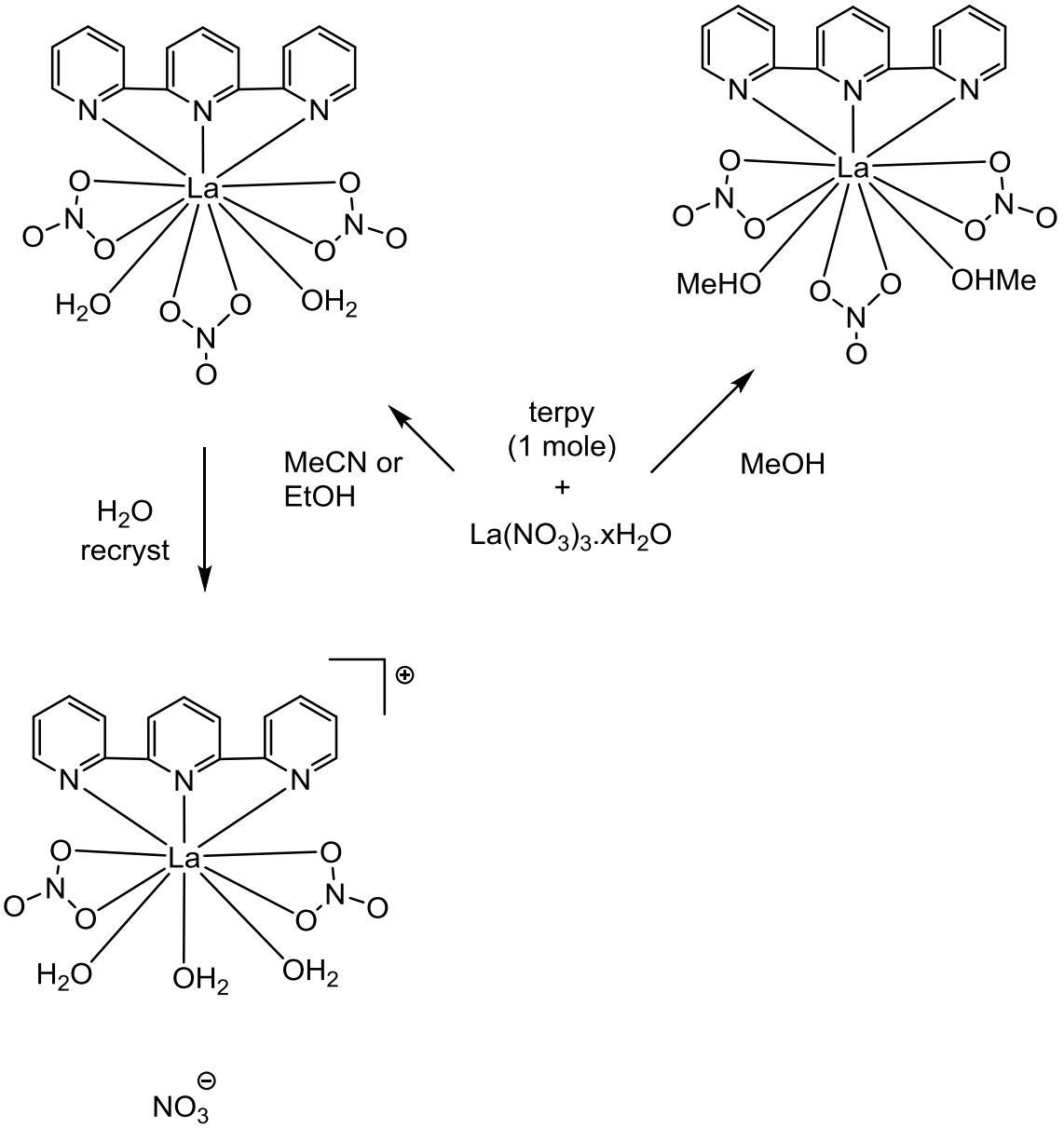


Fig. 14. The effect of solvents on the "[La(terpy)(NO_3)$_3$]"·system

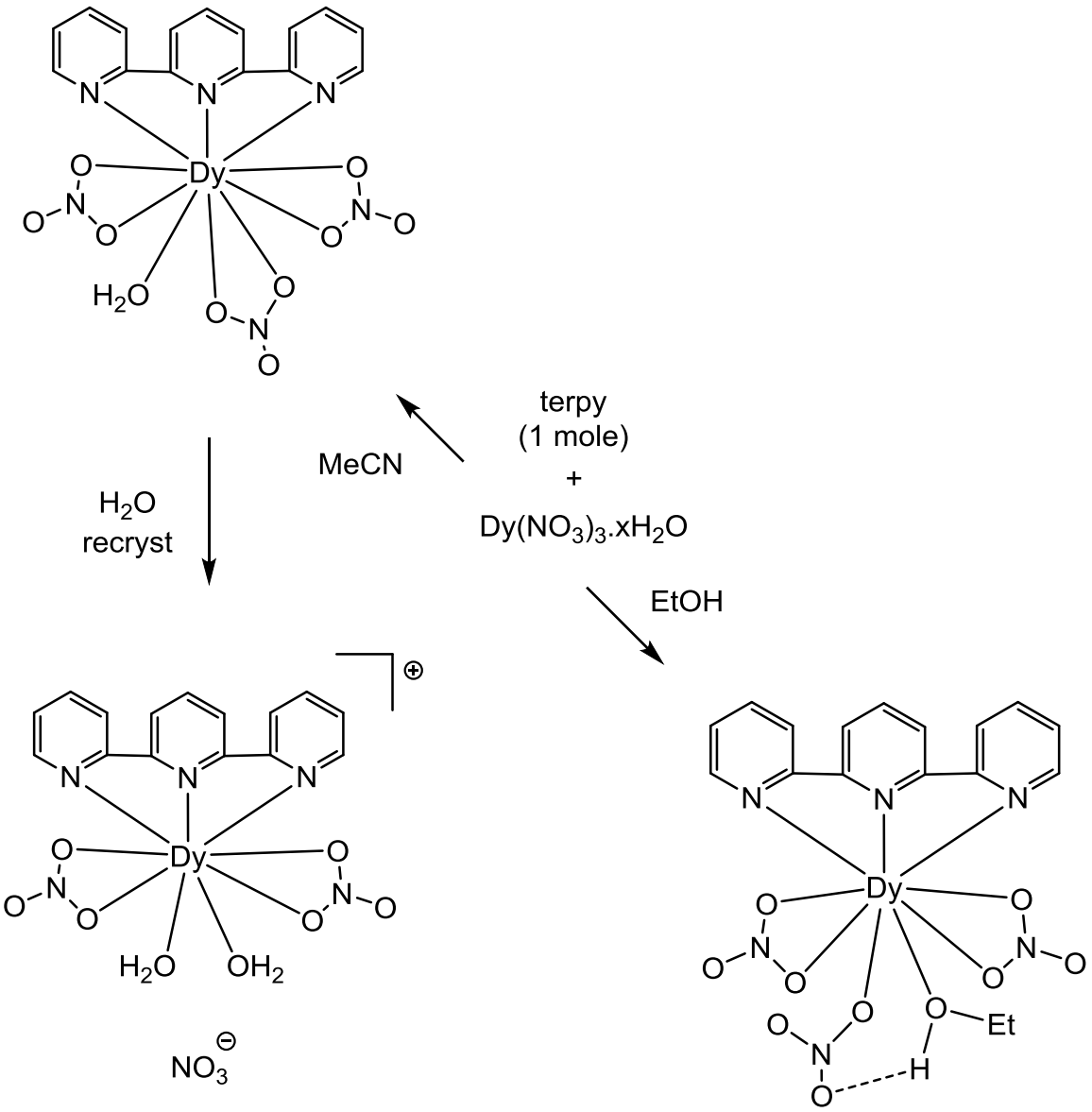


Fig. 15. The effect of solvents on the "[Dy(terpy)(NO_3)$_3$]"·system

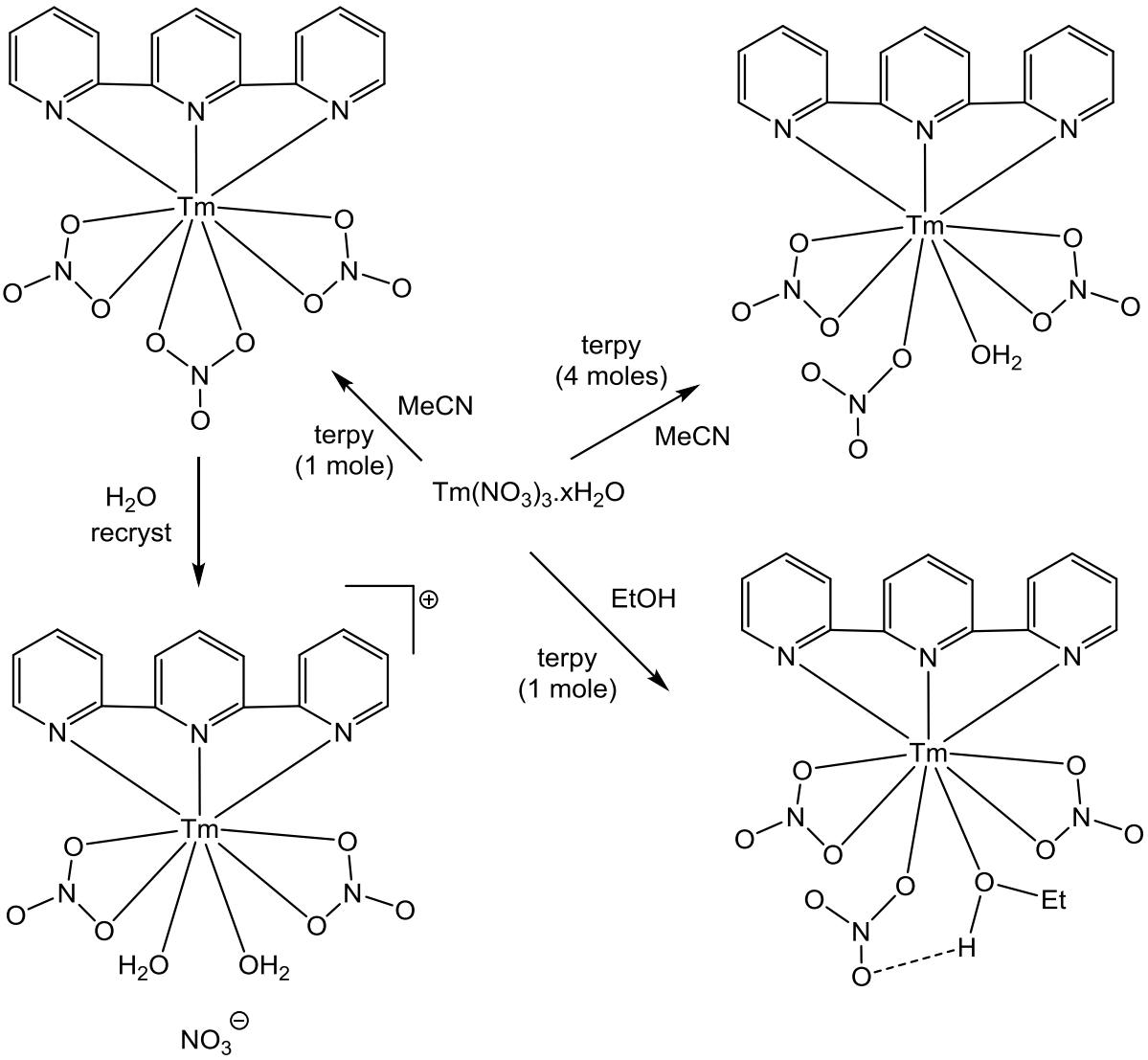


Fig. 16. The effect of solvents on the "[Tm(terpy)(NO_3)$_3$]"·system

6. Complexes of the lanthanide thiocyanates with triphenylphosphine oxide

The triphenylphosphine oxide complexes of the lanthanide thiocyanates appeared to be a case where there was a clear change in coordination number in mid-series. Originally, Cousins and Hart reported [54] the preparation of $[Ln(Ph_3PO)_4(NCS)_3]$ (Ln = La-Sm except Pm) and $[Ln(Ph_3PO)_3(NCS)_3]$ (Ln = Sm-Lu, Y). They noted that, using a 6:1 ligand to $Sm(NCS)_3$ ratio, the product obtained was $[Sm(Ph_3PO)_4(NCS)_3]$, whilst a 2:1 ratio gave $[Sm(Ph_3PO)_3(NCS)_3]$. We found that it was also possible to obtain both the 4:1 and 3:1 complexes for Eu, Gd and Tb [55].

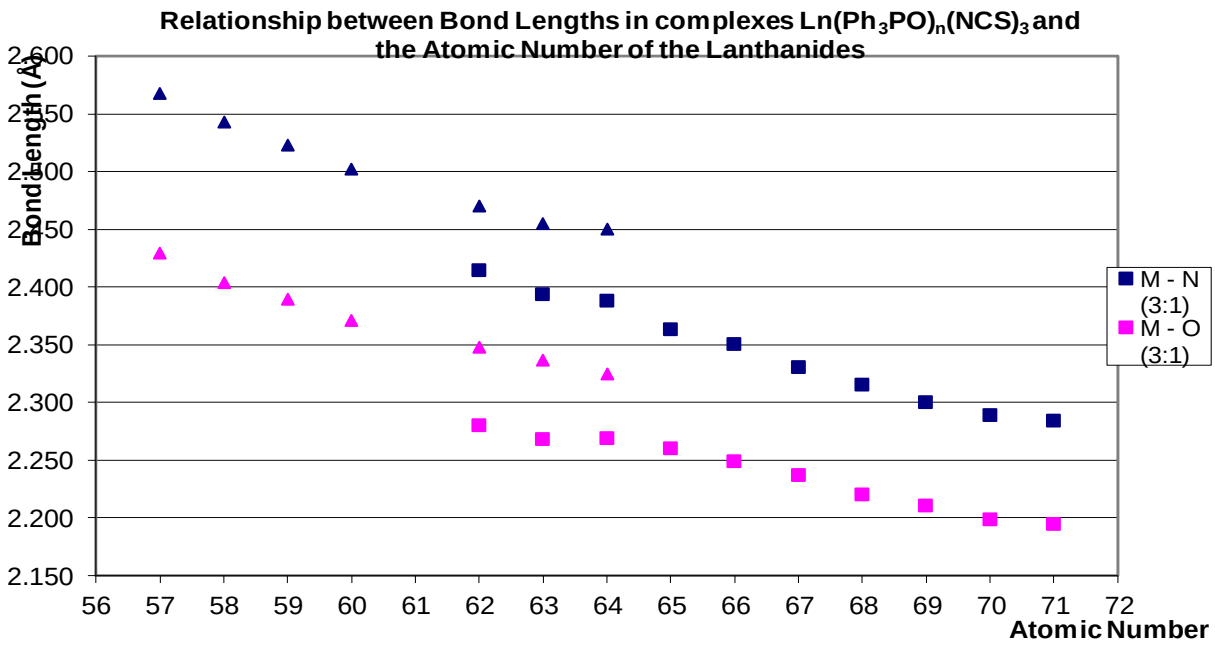


Fig. 17. Ln-N and Ln-O bond lengths for the lanthanide series $[Ln(Ph_3PO)_4(NCS)_3]$ (Ln = La-Sm except Pm) and $[Ln(Ph_3PO)_3(NCS)_3]$ (Ln = Sm-Lu, Y). The error bar on each point on the graph is of the order of ±0.005 Å.

When we carried out this study, no other structures had been reported, but subsequently the structures of $[Nd(Ph_3PO)_4(NCS)_3]$ and $[Tb(Ph_3PO)_3(NCS)_3]$ have been described by others [56, 57].

The series of $[Ln(Ph_3PO)_4(NCS)_3]$ complexes is isostructural (Fig. 18), with what can be described as a capped octahedral coordination geometry around the metal, with the three thiocyanates occupying the three *fac* sites of the capped octahedral face. Considered in isolation, this might be thought due to the phosphine oxides being the bulkier ligands, but that is not the case, as the structures of the 3:1 complexes show.

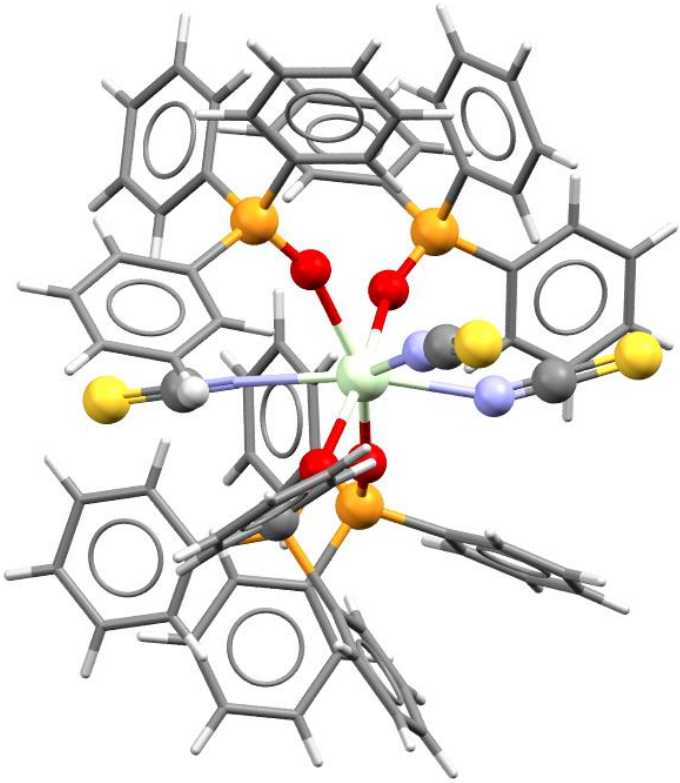


Fig. 18. The structure of $[Pr(Ph_3PO)_4(NCS)_3]$ to illustrate the molecular structures of the of $[Ln(Ph_3PO)_4(NCS)_3]$ series

On passing from $[La(Ph_3PO)_4(NCS)_3]$ to $[Gd(Ph_3PO)_4(NCS)_3]$, the average Ln-O distance decreases from 2.429 to 2.325 Å, a decrease of 0.104 Å, whilst the average Ln-N distance decreases from 2.568 to 2.450 Å, a decrease of 0.108 Å, both of these corresponding closely to the change of ca. 0.10 Å predicted from crystal radii considerations [50].

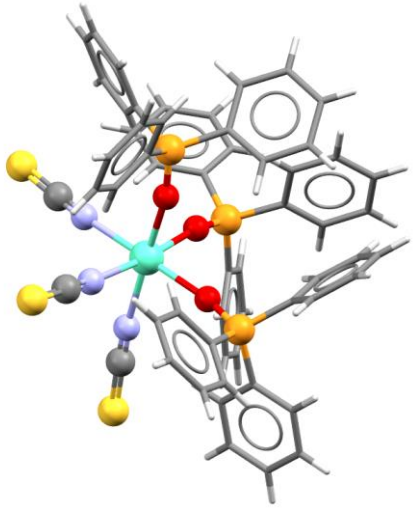


Fig. 19. The structure of $[Eu(Ph_3PO)_4(NCS)_3]$ to illustrate the molecular structures of the of $[Ln(Ph_3PO)_3(NCS)_3]$ series

Similarly, the series of $[Ln(Ph_3PO)_3(NCS)_3]$ complexes is isostructural. The facial isomer is formed by $[Ln(Ph_3PO)_3(NCS)_3]$ (Ln = Y, Sm-Lu), indicating that the steric demands of the three phenyl groups are relatively low; unlike the case in complexes of triphenylphosphine itself, the bulky phenyl rings are so far away from the metal that this does not affect the coordination geometry. Thus in the erbium complex, the N-Er-N and O-Er-O angles fall in the range 85.6 – 99.0°, with no indication of the phosphine oxide or thiocyanate ligands having greater steric influence. The contraction of the bond length from $[Sm(Ph_3PO)_3(NCS)_3]$ to $[Lu(Ph_3PO)_3(NCS)_3]$ is of 0.115 Å for the Ln-N bond length and of 0.104 Å in the Ln-O distance. These contractions may be compared with a contraction of 0.097 Å in the crystal radii [50], which lies just below the two distances given above.

Isolation of both the 4:1 and 3:1 complexes $[Ln(Ph_3PO)_4(NCS)_3]$ and $[Ln(Ph_3PO)_3(NCS)_3]$ for the four lanthanides samarium, europium, gadolinium and terbium facilitates a direct measure of the effect in change of coordination number upon bond length (Table 3). The decrease in Ln-N and Ln-O bond length between the seven and six- coordinate complexes lies between 0.047 and 0.071 Å; this corresponds well to the difference in ionic radius in seven and six coordination given by Shannon [50].

Table 3. Average bond lengths in $[Ln(Ph_3PO)_4(NCS)_3]$ and $[Ln(Ph_3PO)_3(NCS)_3]$ (Ln = Sm-Tb)

		Sm	d (Å)	Eu	d (Å)	Gd	d (Å)	Tb	d (Å)
$[M(Ph_3PO)_4(NCS)_3]$	M-O	2.348		2.337		2.325		2.307	
$[M(Ph_3PO)_3(NCS)_3]$	M-O	2.298	0.050	2.282	0.055	2.269	0.056	2.260	0.047
$[M(Ph_3PO)_4(NCS)_3]$	M-N	2.470		2.455		2.450		2.431	
$[M(Ph_3PO)_3(NCS)_3]$	M-N	2.399	0.071	2.390	0.065	2.388	0.062	2.363	0.068

The fact that both the tris- and tetrakis- complexes can be isolated for these four metals indicates that both species coexist in equilibrium in solution, an equilibrium that can be displaced by adding extra ligand.

A related phenomenon exists for the aqua ions $[Ln(H_2O)_n]^{3+}$ (n = 8, 9). For species with n = 9, trigonal prismatic $[Ln(OH_2)_9]^{3+}$ ions predominate for the early metals (Ln = La-Nd), whilst for species with n = 8, square antiprismatic eight-coordinate $[Ln(OH_2)_8]^{3+}$ ions are found for yttrium and the later lanthanides (Ln = Gd-Lu). A mixture of eight- and nine-coordinate species exists for Ln = Pm-Eu. The $[Ln(OH_2)_9]^{3+}$ ions can be isolated for all metals as certain

salts, like the ethylsulfate and bromate; in a more extreme example, crystals of the hydrated lanthanide perchlorates all contain octahedral $[Ln(OH_2)_6]^{3+}$ ions [57].

7. Some conclusions

We have learned some lessons from this study, none new, but salutary reminders nonetheless.

In the series of coordination complexes discussed in this review coordination numbers of between 6 and 11 have been observed, with coordination number of 9 and 10 being perhaps the most common. The steric bulk and flexibility of the ligands plays a key role in determining the resultant coordination number and geometry.

Importantly, discontinuities can arise at any point in the lanthanide series, so where possible each of the elements should be examined in any particular study. Frequently these appear at the extremes; it is worth remembering that the difference in ionic radius between lanthanum and cerium is greater than for any other pair of adjacent elements [50]. Two or more species may be in equilibrium in solution and often only one may be isolated, so that the determination of a crystal structure is almost certainly not reflecting the whole story and does not necessarily represent the solution chemistry.

There are often differences between the most abundant species present in solution and that isolated in the solid state. The kinetics and thermodynamics of the reactions are complex, but both aspects need to be considered carefully if anything like the full story is to be understood.

From a purely practical viewpoint, different complexes can be isolated by using different solvents, and the donor/acceptor properties of the solvent are key here. The choice of solvent may be vital in getting crystals suitable for a single-crystal X-ray diffraction study. It is prudent to use multiple diffraction and spectroscopic techniques to analyse the reactions in order to gain a better understanding of the chemistry of the lanthanide elements and their complexes.

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