



Citation for published version:

Chan, L, Cotton, SA, Dickson (nee Harris), J, Platt, AWG, Raithby, PR, Schiffers, S, Tait, A & Warren, JE 2022, 'Structural diversity in the series of lanthanide complexes $[\text{Ln}(\text{Ph}_3\text{PO})_n(\text{NCS})_3]$ ($n = 3, 4$)', *Polyhedron*, vol. 220, 115826. <https://doi.org/10.1016/j.poly.2022.115826>

DOI:

[10.1016/j.poly.2022.115826](https://doi.org/10.1016/j.poly.2022.115826)

Publication date:

2022

Document Version

Peer reviewed version

[Link to publication](#)

Publisher Rights

CC BY-NC-ND

University of Bath

Alternative formats

If you require this document in an alternative format, please contact:
openaccess@bath.ac.uk

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Structural diversity in the series of lanthanide complexes [Ln(Ph₃PO)_n(NCS)₃] (n = 3, 4).

Lawrence Chan^a, Simon A. Cotton^{a,b*}, Joanna Dickson (née Harris)^a, Andrew W. G. Platt^c, Paul R. Raithby^{d*}, Stefanie Schiffrers^d, Alexander Tait^a, John E. Warren^e

^a Uppingham School, Uppingham, Rutland LE15 9QE, U.K.

^b School of Chemistry, University of Birmingham, Birmingham B15 2TT, U.K.

^c School of Justice, Security and Sustainability, Staffordshire University, Leek Road, Stoke on Trent, ST4 2DF, UK

^d Department of Chemistry, University of Bath, Bath, BA2 7AY UK

^e CCLRC Daresbury Laboratory, Daresbury, Warrington WA4 4AD, UK

Received:

Accepted:

Available online:

Keywords: Lanthanides; Lanthanide contraction; Phosphine oxide; Thiocyanate; Crystal structures

Abstract

Two unique series of lanthanide complexes [Ln(Ph₃PO)₄(NCS)₃] (Ln = La-Tb, except Pm) and [Ln(Ph₃PO)₃(NCS)₃] (Ln = Sm-Lu, Y) have been structurally characterised. The isomorphous series [Ln(Ph₃PO)₄(NCS)₃] crystallises in the monoclinic centrosymmetric space group $P2_1/c$, and the metals display a capped octahedral coordination geometry. In contrast, the isomorphous series [Ln(Ph₃PO)₃(NCS)₃] (Ln = Sm-Lu, Y) crystallise in the non-centrosymmetric space group $R\bar{3}$, with the metal displaying an octahedral coordination geometry; the *fac*-isomer being observed in all cases. Intriguingly, for the metals Sm-Tb both the seven and six coordinate complexes can be isolated from the respective synthetic routes suggesting a structural equilibrium in solution. An analysis of the distortions of the ligand polyhedral in the two series using the continuous shape measurement (CShMs) method suggests trends across the series relating to the fit of the ligands with the size of the lanthanide ions.

Introduction

In almost a century since Goldschmidt first enunciated it, the 'lanthanide contraction' has become an essential concept in the chemistry of the 4f metals [1-3] though new insights continue to become apparent [4-5].

There are few structural studies of complexes that show that the same coordination number is maintained across the whole series [6-7], usually there is a reduction in coordination number as the size of the metal ions decreases across the series. We studied the complexes of 2,4,6-tri- α -pyridyl-1,3,5-triazine (tptz) with the lanthanide nitrates, observing very similar coordination behaviour across almost all the series, for all the metals except lutetium [8]. It is apparent that whether there is a change in coordination number and where along the series this change occurs is dependent on the properties of the ligands as well as the size of the metal ions.

We now report a development of our structural studies on the lanthanide contraction and on the properties of lanthanide coordination complexes to include a wider range of mixed ligand systems. In this publication we report full structural data on the complete series of lanthanide (La-

Lu, except Pm) thiocyanate complexes supported by triphenylphosphine oxide ligands together with the structure of the analogous yttrium complex. The majority of these complexes have been synthesised and partly characterised by Cousins and Hart [9], but there is limited structural information. The structures of $[\text{Nd}(\text{Ph}_3\text{PO})_4(\text{NCS})_3]$ [10] and $[\text{Tb}(\text{Ph}_3\text{PO})_3(\text{NCS})_3]$ [11] have been reported by others as has that of $[\text{Eu}(\text{Ph}_3\text{PO})_3(\text{NCS})_3]$, present in the mixed crystal $[\text{Eu}(\text{Ph}_3\text{PO})_3(\text{NCS})_3] \cdot [\text{Eu}(\text{Ph}_3\text{PO})_3(\text{NCS})_2(\text{NO}_3)]$ [12].

Experimental

Materials

The hydrated lanthanide chlorides, potassium thiocyanate, ammonium thiocyanate, triphenylphosphine oxide and solvents were obtained as commercial products (Aldrich) and were used without purification.

IR spectra were obtained using a Perkin Elmer, Universal ATR Sampling Accessory, Spectrum 100 FT-IR Spectrometer without additives.

Synthesis of $[\text{Ln}(\text{Ph}_3\text{PO})_4(\text{NCS})_3]$ and $[\text{Ln}(\text{Ph}_3\text{PO})_3(\text{NCS})_3]$ series and of $[\text{Y}(\text{Ph}_3\text{PO})_3(\text{NCS})_3]$

The complexes in the two series were synthesised, following literature procedures [9]. Here the method used to prepare the tetrakis-triphenylphosphine oxide series Ln = La-Tb, except Pm, is illustrated for the synthesis of $[\text{Pr}(\text{Ph}_3\text{PO})_4(\text{NCS})_3]$. Hydrated $\text{PrCl}_3 \cdot 7\text{H}_2\text{O}$ (0.11 g; 0.29 mmol) was dissolved in ethanol (5 ml) and mixed with a solution of KNCS (0.10 g; 1.03 mmol) in ethanol (5 ml). After standing, the precipitate of KCl was removed by filtration and the solution then warmed and added to a hot solution of Ph_3PO (0.37 g; 1.33 mmol) in ethanol (4 ml). Green crystals formed on cooling. The method for the tris-triphenylphosphine oxide series Ln = Sm-Lu is exemplified by the synthesis of $[\text{Sm}(\text{Ph}_3\text{PO})_3(\text{NCS})_3]$. Hydrated $\text{SmCl}_3 \cdot 6\text{H}_2\text{O}$ (0.10 g, 0.29 mmol), NH_4NCS (0.10 g, 1.0 mmol) and Ph_3PO (0.28 g, 1.0 mmol) were dissolved in warm methanol. Crystals were obtained through slow evaporation of the solvent from the solution.

The complexes were characterised initially by comparison of their IR spectra with literature values [9] and by subsequent single-crystal X-ray diffraction analysis.

Single crystal X-ray crystallography

Crystals are obtained from the mother liquor and mounted on a glass fibre with oil and transferred to a diffractometer. The crystal data, data collection parameters, and structure solution and refinement details for the crystal structures determined are summarised in the supporting information (Tables S2-4; compounds $[\text{Ln}(\text{Ph}_3\text{PO})_4(\text{NCS})_3]$ designated **La4 – Tb4**, $[\text{Ln}(\text{Ph}_3\text{PO})_3(\text{NCS})_3]$ designated **Sm3-Lu3**). Data collections were carried out on a Nonius Kappa CCD diffractometer, using graphite monochromated Mo K_α radiation, on a Bruker AXS SMART diffractometer, at Station 9.8 of the CCLRC Daresbury Laboratory and on an Oxford Diffraction Gemini A Ultra also using graphite monochromated Mo K_α radiation. The first two diffractometers were equipped with an Oxford Cryostream cooling apparatus (600 and 700) [13], whereas the last one has a CryojetXL cooling device. The structures were solved using Sir92 [14], SHELX-86 [15] and refined by full-matrix least-squares based on F^2 using SHELXL-97 [16]. All non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogen atoms were placed in idealised positions and allowed to ride on the relevant carbon atoms. Isotropic displacement parameters for the hydrogen atoms were set at $1.2U_{\text{eq}}$ of the relevant carbon atom. Refinements were continued until convergence was reached and the residual electron density maps showed no chemically sensible residual features.

Results and Discussion

Preparation

The series of lanthanide complexes $[\text{Ln}(\text{Ph}_3\text{PO})_4(\text{NCS})_3]$ ($\text{Ln} = \text{La-Tb}$, except Pm) and $[\text{Ln}(\text{Ph}_3\text{PO})_3(\text{NCS})_3]$ ($\text{Ln} = \text{Sm-Lu}$, Y) were prepared following the literature method [9] using the appropriate hydrated lanthanide trichloride with a thiocyanate salt and triphenylphosphine oxide in ethanol or methanol. The crystalline products were obtained by slow evaporation of the mother liquor and their IR spectra used to confirm the formation of the expected products. The spectra of the complexes were found to be generally in very good agreement (Supporting Information, Table S1) with those reported by Cousins and Hart [9]. The two series of complexes can be distinguished by the spectra in the $\nu(\text{CN})$ region. The *tris*-complexes contain two bands in the region $2000\text{-}2100\text{ cm}^{-1}$, a main band with resolved shoulder as expected for a *fac*- $\text{ML}_3(\text{NCS})_3$ system (c.f. *fac*- $\text{MoL}_3(\text{CO})_3$ [17]), whereas the *tetrakis* complexes give rise to three bands, a split doublet with a resolved shoulder to higher frequency, consistent with the environment of lower symmetry. The spectra are sufficiently different to enable them to be distinguished in a mixture of crystals of $[\text{Ln}(\text{Ph}_3\text{PO})_3(\text{NCS})_3]$ and $[\text{Ln}(\text{Ph}_3\text{PO})_4(\text{NCS})_3]$.

Cousins and Hart [9] prepared $[\text{Ln}(\text{Ph}_3\text{PO})_4(\text{NCS})_3]$ ($\text{Ln} = \text{La-Sm}$ except Pm) and $[\text{Ln}(\text{Ph}_3\text{PO})_3(\text{NCS})_3]$ ($\text{Ln} = \text{Sm-Lu}$). They found that in the case of samarium, using a 2:1 ligand to $\text{Ln}(\text{NCS})_3$ ratio gave the tris-complex, but a 6:1 ratio gave the tetrakis- Ph_3PO -complex. We have repeated these syntheses using 3:1 and 4:1 ratios, respectively. We have also found that by following this procedure both the 4:1 and 3:1 complexes may be obtained for Eu, Gd and Tb. We note that the crystal structures of $[\text{Nd}(\text{Ph}_3\text{PO})_4(\text{NCS})_3]$ [10] and $[\text{Tb}(\text{Ph}_3\text{PO})_3(\text{NCS})_3]$ [11] have already been reported but we have undertaken a comprehensive set of single crystal X-ray structure determinations for the two series under the same experimental conditions, including independent determinations of $[\text{Nd}(\text{Ph}_3\text{PO})_4(\text{NCS})_3]$ and $[\text{Tb}(\text{Ph}_3\text{PO})_3(\text{NCS})_3]$, in order to obtain a full set of comparative data for the two series. We have also determined the structure of the analogous yttrium(III) complex $[\text{Y}(\text{Ph}_3\text{PO})_3(\text{NCS})_3]$ as a comparison.

Crystal structures of the complexes $[\text{Ln}(\text{Ph}_3\text{PO})_4(\text{NCS})_3]$ ($\text{Ln} = \text{La-Tb}$, except Pm)

The $[\text{Ln}(\text{Ph}_3\text{PO})_4(\text{NCS})_3]$ complexes are isomorphous and isostructural. They crystallise in the monoclinic space group $P2_1/c$ with one molecule in the asymmetric unit. In the complexes the metal ions are all seven coordinate with three thiocyanate ligands and four triphenylphosphine oxide ligands. Two of the thiocyanates are essentially linear with Ln-N-C and N-C-S angles above 170° , while the third thiocyanate ligand exhibits a slight bend at the coordinated N-atom with the Ln-N-C angle across the series ranging from $153.4(2) - 157.1(3)^\circ$. In each complex the sulphur atom of this bent thiocyanate is associated with the shortest intermolecular contact in the structure, a contact to a phenyl hydrogen atom in an adjacent molecule, at between $0.27\text{-}0.30\text{ \AA}$ less than the sum of the van der Waals radii. These S...H contact distances are listed in Table S5 (supporting information). Since the bent thiocyanate is orientated to lean towards this H-atom it suggests that this is a favourable non-covalent interaction helping to stabilise the crystal structures. There are no other intermolecular interactions that are shorter than 0.1 \AA less than the sum of the van der Waals radii and these are not considered significant.

We now describe the general molecular features of the series of complexes using $[\text{Pr}(\text{Ph}_3\text{PO})_4(\text{NCS})_3]$ (Fig. 1) as an example. The seven coordinate Pr ion displays a capped octahedral coordination geometry, with the three thiocyanates occupying the three *fac*-sites of the capped octahedral face. The average bond length of Pr-N is 2.523 \AA and 2.389 \AA for Pr-O. Two of the Pr-N-C

angles are nearly linear with $170.7(3)^\circ$ and $172.0(3)^\circ$, whereas the third is slightly more bent ($154.4(3)^\circ$) as discussed above.

On passing from $[\text{La}(\text{Ph}_3\text{PO})_4(\text{NCS})_3]$ to $[\text{Gd}(\text{Ph}_3\text{PO})_4(\text{NCS})_3]$, the average Ln-O distance decreases from 2.429 \AA to 2.325 \AA , a decrease of 0.104 \AA , whilst the average Ln-N distance decreases from 2.568 \AA to 2.450 \AA , a decrease of 0.108 \AA , both of these corresponding closely to the change of ca. 0.10 \AA predicted from crystal radii considerations [18].

Our crystallographic results for $[\text{Nd}(\text{Ph}_3\text{PO})_4(\text{NCS})_3]$ are in extremely good agreement with bond parameter data found in the previous structure determination of the complex, the average Nd-N distance being 2.502 \AA (2.503 \AA) [10], and the average Nd-O distance being 2.371 \AA (2.375 \AA) [10] with the slight decrease of ours compared to theirs being compatible with the temperature differences; 100 K compared to 110 K [10].

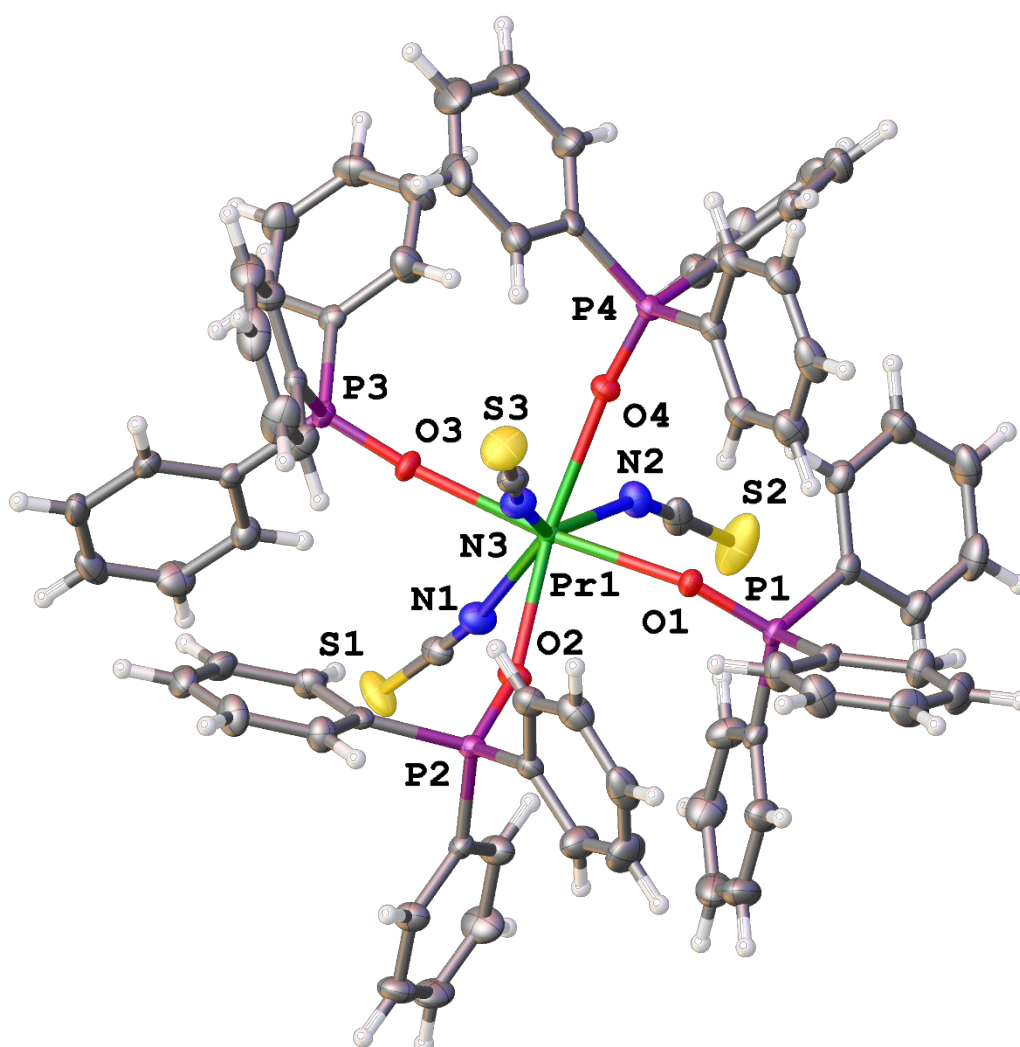


Fig. 1 The molecular structure of $[\text{Pr}(\text{Ph}_3\text{PO})_4(\text{NCS})_3]$ with 50 % displacement ellipsoids.

The assignment of the capped octahedral coordination geometry (COC-7) was confirmed by an analysis using the continuous shape measurement (CShMs) method [19] implemented using version 2.1 of the *SHAPE* program [20]. In the method the atomic coordinates of the atoms in the coordination polyhedron surrounding the central metal are compared to a series of idealised polyhedra appropriate for a given coordination number. In this way the method calibrates the overall distance of the atoms to those of the reference shape in the same position and with the same size and orientation using a single dimensionless parameter, *S*. A value of *S*=0 for a given polyhedron shows that it has exactly the same shape as the reference polyhedron. The larger the value of *S* the greater is the deviation from the idealised geometry. When several idealised geometries are possible for a given coordination number the *S* values for the coordination polyhedron to the polyhedral of the idealised geometries can be compared to establish which has the best fit. If there is a significant distortion from the idealised shape the comparative *S* values indicate what form the distortion to another idealised geometry may take. For the series [Ln(Ph₃PO)₄(NCS)₃] (La-Tb except Pm) all the complexes most closely fit to the capped octahedron (COC-7) with *S* values ranging from *S* = 1.39 (La) to 1.51 (Tb). The next best fit to an idealised polyhedron is to the capped trigonal prism (CTPR-7) where the *S* values range from *S* = 1.61 (La) to 1.81 (Gd). Given the different steric requirements of the NCS and OPPh₃ ligands in these complexes a significant distortion from an idealised ligand polyhedron is not surprising, and the energy difference between a capped octahedral and a capped trigonal prismatic idealised geometry is quite small.

The seven coordinated structure is quite common for LnL₄X₃ systems, such as the thf complexes [Yb(NCS)₃(thf)₄] [21, 22], [EuCl₃(thf)₄] and [GdCl₃(thf)₄] [23, 24], [NdBr₃(thf)₄] [25] and [PrI₃(thf)₄] [26]. In contrast to the [Ln(NCS)₃(thf)₄]₂ (Ln = Nd, Er) [22], the complexes described here are all monomers, reflecting the increased steric bulk of Ph₃PO, if compared with thf. They share with the Pr complex the feature of one Pr-NC linkage being noticeably more bent than the others, thus in the La complex the angles are 153.42(19)°, 170.85(18)° and 171.04(18)°, and in the Tb complex 156.7(2)°, 170.70(15)° and 172.81(16)°.

In the seven coordinate [La((Me₂N)₃PO)₄(NCS)₃], the average La-O and La-N distances of 2.433 Å and 2.581 Å, respectively [27] are closely comparable to the corresponding values of 2.429 Å and 2.568 Å in [La(Ph₃PO)₄(NCS)₃]. In the seven coordinate [Nd(Ph₃PO)₄(η¹-OTf)(η²-OTf)] OTf (OTf = triflate), Nd-OPPh₃ distances average 2.323 Å, rather less than the value of 2.371 Å in [Nd(Ph₃PO)₄(NCS)₃], doubtless due to the small bite of the bidentate triflate permitting closer approach of the other ligands [28].

Crystal structures of the complexes [Ln(Ph₃PO)₃(NCS)₃] (Ln = Sm-Lu, Y)

All the 3:1 complexes crystallise in the non-centrosymmetric trigonal space group *R*3 with one and one third molecules in the asymmetric unit, the one third of the molecule lying on a crystallographic three-fold axis. Both molecules display a *fac*-octahedral coordination with three linear thiocyanates and three triphenylphosphine oxide ligands. The shortest intermolecular contact is an interaction between the sulphur atom of one of the thiocyanate ligands and a phenyl hydrogen atom of a triphenylphosphine oxide ligand in an adjacent molecule. These contacts are between 0.27 – 0.16 Å shorter than the sum of the van der Waals radii ranging from 2.74 – 2.84 Å (See Table S5, supporting information), and are the only interactions significantly shorter than the sum of the van der Waals radii for the interacting atoms. These distances are a little longer than the similar interactions found for the [Ln(Ph₃PO)₄(NCS)₃] series and, for these six coordinate complexes the thiocyanate ligands all remain essentially linear.

These complexes adopt the same geometry as found for *fac*-[Fe(Ph₃PO)₃(NCS)₃], a complex with a significantly smaller metal ion [29]. In contrast to the Fe structure, however, both molecules in the structure of the lanthanide series have the same chirality. Within each crystal structure the two independent molecules have almost the same geometry (Fig. 2). The O-Ln-N angle show some deviation from the idealised octahedral symmetry, this indicates a twist along the threefold axis in the symmetry constrained molecule and a twist along the pseudo threefold axis in the unconstrained molecule.

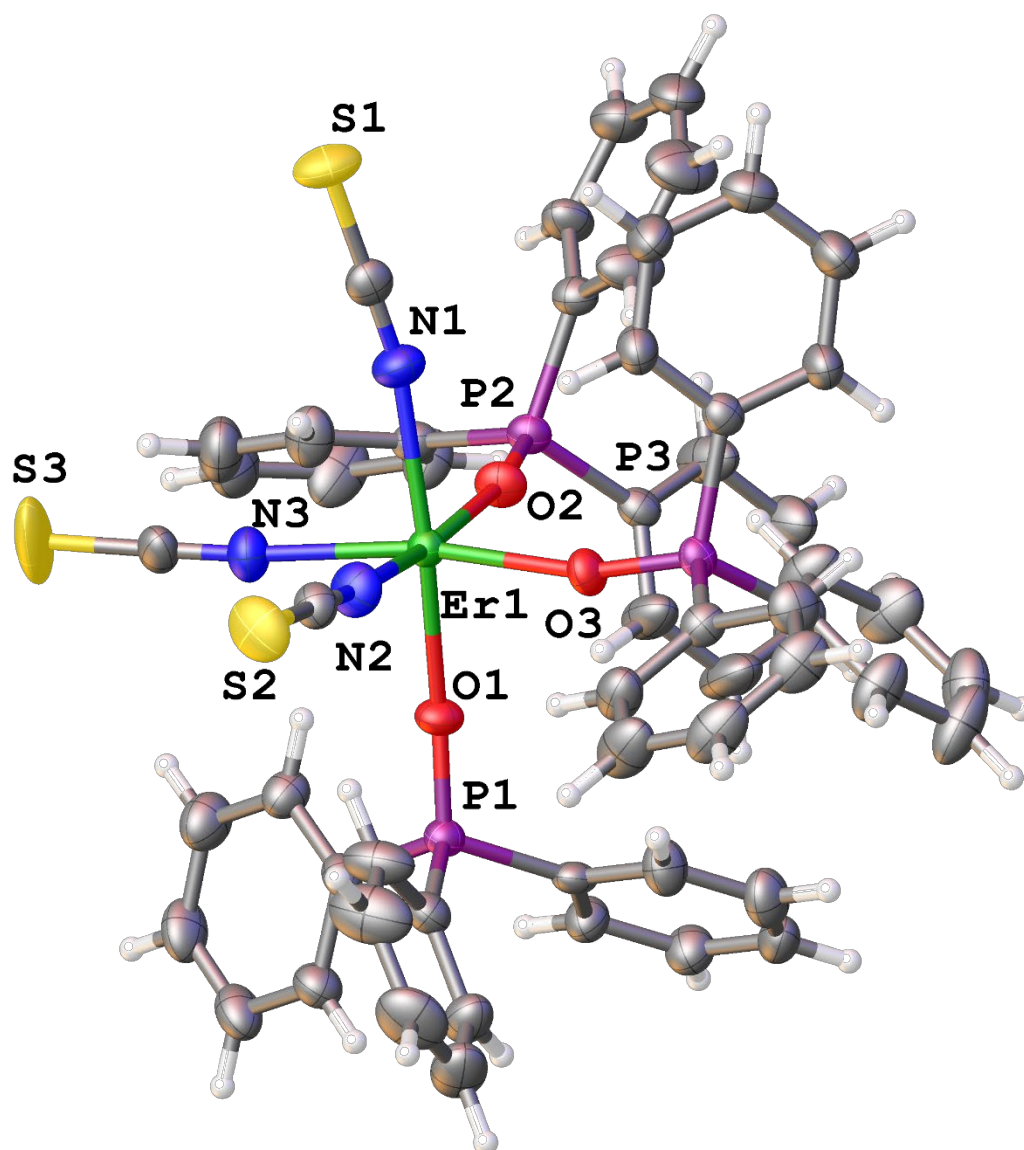


Fig. 2 The structure of the unconstrained molecule of [Er(Ph₃PO)₃(NCS)₃] with 50% displacement ellipsoids

A description of the bond parameters for the two independent molecules is provided using the erbium structure, [Er(Ph₃PO)₃(NCS)₃], as an example. The fully unconstrained molecule has average bond length of Er-N(av). 2.321 Å and Er-O(av). 2.213 Å, while in the symmetry constrained

molecule the Er-N bond length is 2.314(4) Å and the Er-O distance is 2.221(2) Å. The N-C-Ln coordination is nearly linear, sample values for the Er complex being 167.8(3)°, 174.2(4)° for the first molecule and 175.4(3)° and 168.5(3)° for the second molecule. For the Tb complex the bond parameters are very similar to those observed in the previous structure determination [11]. The average Tb-N distance being 2.363 Å (2.355 Å [11]), and the average Tb-O distance being 2.260 Å (2.267 Å [11]). Similarly, when the bond parameters for our determination of [Eu(Ph₃PO)₃(NCS)₃] are compared to the values reported in the mixed complex [Eu(Ph₃PO)₃(NCS)₃].[Eu(Ph₃PO)₃(NCS)₂(NO₃)] there is also good agreement [12]. The average Eu-N distance is 2.393 Å (2.397 Å [12]), and the average Eu-O distance is 2.269 Å (2.292 Å [12]).

The coordination geometries in the series [Ln(Ph₃PO)₃(NCS)₃] (Ln = Sm-Lu, Y) have also been analysed using the SHAPE software [20]. For the unconstrained complexes in each crystal structure the *S* values obtained compared to the completely regular octahedral geometry (OC-6) ranged from 1.09 (Sm) to 0.61 (Lu) while the alternate idealised geometry, the trigonal prism (TPR-6), had *S* values of the order of 10 and thus could be eliminated from consideration. There is a fairly regular decrease in the value of *S* in going from Sm to Lu across the lanthanide series that suggests that the later (smaller) lanthanide (III) ions show less of a distortion from a regular octahedral geometry than do the larger ones.

The average Tb-O distance of 2.260 Å in [Tb(Ph₃PO)₃(NCS)₃] compares closely with the value of 2.262 Å in the similarly six coordinate [Tb(Ph₃PO)₄Cl₂]⁺ ion [30]; similarly the average Yb-O distance of 2.198 Å in six coordinate [Yb(Ph₃PO)₃(NCS)₃] is close to the average of 2.205 Å in the [Yb(Ph₃PO)₄Cl₂]⁺ ion [30]. In the six coordinate [Lu(η¹-OTf)₂(Ph₃PO)₄]⁺OTf Lu-OPPh₃ distances average 2.183 Å [28], close to the value of 2.194 Å in [Lu(Ph₃PO)₃(NCS)₃].

For completeness, we also determined the structure of the analogous Group 3 Y(III) complex (Fig. 3). The structure is isomorphous with the [Ln(Ph₃PO)₃(NCS)₃] (Ln = Sm-Lu) series and the average Y-O and Y-N bonds are 2.198 Å and 2.293 Å, respectively, for the octahedral complex. The calculated *S* value for this complex is 0.95, similar to that calculated for Eu (*S* = 0.97), Gd (*S* = 0.93) and Tb (*S* = 1.00).

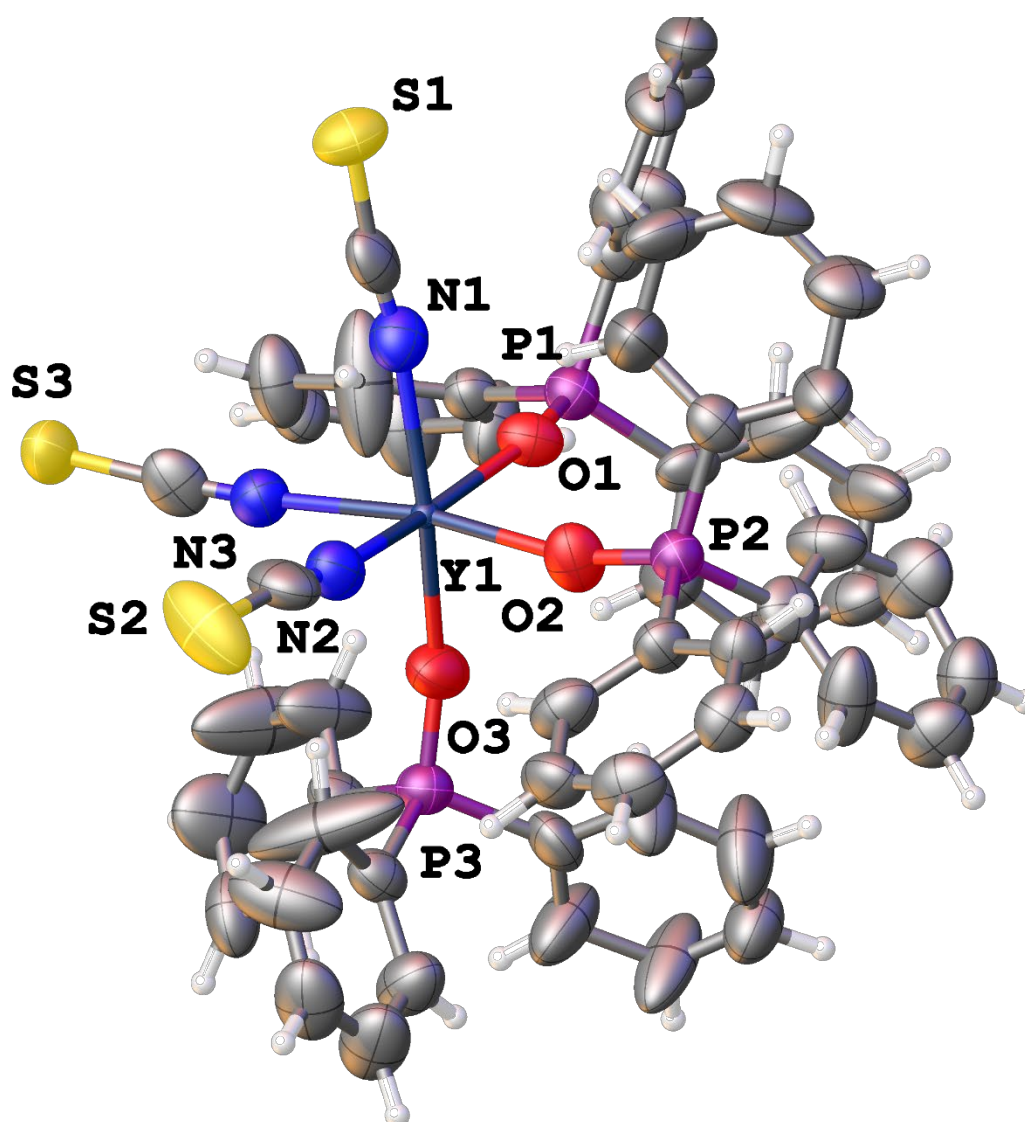


Fig. 3 The structure of the unconstrained molecule of $[\text{Y}(\text{Ph}_3\text{PO})_3(\text{NCS})_3]$ with the displacement ellipsoids drawn with 50% probability.

Comparison of the structures of $[\text{Ln}(\text{Ph}_3\text{PO})_4(\text{NCS})_3]$ with $[\text{Ln}(\text{Ph}_3\text{PO})_3(\text{NCS})_3]$

The presence of the facial isomer of $[\text{Ln}(\text{Ph}_3\text{PO})_3(\text{NCS})_3]$ suggests that the steric demands of the three phosphine oxide ligands are relatively low, unlike the case in complexes of triphenylphosphine itself. In the phosphine oxides 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.

In contrast, the isolation of both *fac*- and *mer*- $[\text{Ln}((\text{Me}_2\text{N})_3\text{PO})_3\text{Cl}_3]$ suggests roughly equal steric demands for chloride and this tertiary phosphine oxide [31, 32] whilst $[\text{Ln}(\text{Ph}_3\text{PO})_3\text{Cl}_3] \cdot 0.5\text{Me}_2\text{CO}$ (Ln = La, Ce) have been found to have meridional structures [29], implying

that Ph_3PO is more bulky than a chloride ligand. *Mer*-isomers are the rule in *mer*- $[\text{Sc}(\text{thf})_3\text{Cl}_3]$ [33] and *mer*- $[\text{Ln}(\text{thf})_3\text{Cl}_3]$ ($\text{Ln} = \text{Yb}, \text{Lu}$) [34], as well as in *mer*- $[\text{YbBr}_3(\text{thf})_3]$ [35].

The contraction of the bond length from $[\text{Sm}(\text{Ph}_3\text{PO})_3(\text{NCS})_3]$ to $[\text{Lu}(\text{Ph}_3\text{PO})_3(\text{NCS})_3]$ is 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 [18] in the crystal radii, which lies slightly below the two distances above. The distances in the iron complex $[\text{Fe}(\text{Ph}_3\text{PO})_3(\text{NCS})_3]$ are nearly identical with 2.022 Å for Fe-N(av). and 2.024 Å for Fe-O(av). The complexes $[\text{Ln}(\text{Ph}_3\text{PO})_4(\text{NCS})_3]$ and $[\text{Ln}(\text{Ph}_3\text{PO})_3(\text{NCS})_3]$ ($\text{Sm}, \text{Gd}, \text{Eu}, \text{Tb}$) permit direct assessment of the effect in change of coordination number upon bond length. The decrease in Ln-N and Ln-O bond length between the seven and six-coordinate complexes lies between 0.047 Å and 0.071 Å, closely corresponding to the difference in ionic radius in seven and six coordination given by Shannon [36].

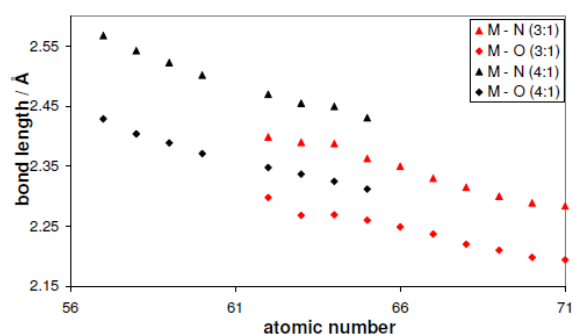


Fig. 4 Relationship between the bond lengths in complexes $[\text{Ln}(\text{Ph}_3\text{PO})_n(\text{NCS})_3]$ ($n = 3, 4$) and the atomic number of the lanthanides

A graph of average Ln-N and Ln-O bond length against atomic number for the two series of complexes (Fig. 4) shows the characteristic relationship found in ionic radii of the lanthanide ions. The lanthanide contraction involves a decrease of 16% in the ionic radius of the Ln^{3+} ion on traversing the series from La to Lu. Most commonly this is accompanied by a change in coordination number, though exceptions include the familiar isostructural ten coordinated $[\text{Ln}(\text{bipy})_2(\text{NO}_3)_3]$ and $[\text{Ln}(\text{phen})_2(\text{NO}_3)_3]$ [37], and the hydrated bromates and ethylsulphates, which all contain $[\text{Ln}(\text{OH}_2)_9]^{3+}$ ions [38, 39]. In contrast, the thiocyanate complexes described here demonstrate the pattern familiar from binary compounds such as the halides and oxides, where coordination numbers are determined by packing ligands round the central metal ion. What is unusual in these series, however, is that around the changeover point (Sm-Tb) there are clearly equilibria involving the presence of six- and seven-coordinate species in solution for certain metal ions, and that both complexes are isolable.

A comparison of the SHAPE parameters calculated using the continuous shape measurement method [19], as described above, is also informative (Table S6). A plot of the S values for the 7-coordinate geometry COC-7 for the $[\text{Ln}(\text{Ph}_3\text{PO})_4(\text{NCS})_3]$ ($\text{Ln} = \text{La-Tb}$, except Pm) and the 6-coordinate geometry OC-6 $[\text{Ln}(\text{Ph}_3\text{PO})_3(\text{NCS})_3]$ ($\text{Ln} = \text{Sm-Lu}$) series are shown in Fig. 5.

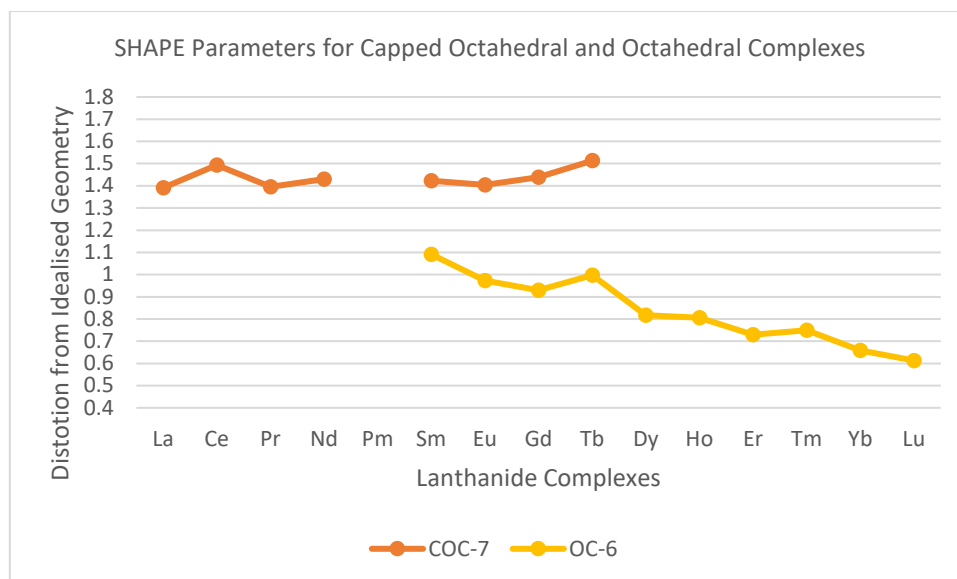


Fig. 5. A plot of the dimensionless continuous shape measurement parameter, S , for the 7-coordinate capped octahedral and 6-coordinate octahedral complexes showing the distortions from the idealised geometries across the series.

For the series $[\text{Ln}(\text{Ph}_3\text{PO})_4(\text{NCS})_3]$ ($\text{Ln} = \text{La-Tb}$, except Pm) there is little evidence of a trend in the S parameter, perhaps because of calibrating all the distances between the coordination polyhedron of the complex and the reference polyhedron into a single number. However, there is a slight upward trend in S for the Gd and Tb complexes that, perhaps, suggests that the 7-coordinate geometry is becoming less favourable. There is a more pronounced downward trend for the octahedral complexes in the series $[\text{Ln}(\text{Ph}_3\text{PO})_3(\text{NCS})_3]$ ($\text{Ln} = \text{Sm-Lu}$) in moving from Sm to Lu . This suggests that an undistorted octahedral arrangement of the three NCS and the three OPPh_3 ligands is a better fit for the smaller lanthanide ions.

Conclusion

Our results show that the complexes $[\text{Ln}(\text{Ph}_3\text{PO})_4(\text{NCS})_3]$ ($\text{Ln} = \text{La-Tb}$, except Pm) form an isomorphous series with capped octahedral seven coordination, whilst the series $[\text{Ln}(\text{Ph}_3\text{PO})_3(\text{NCS})_3]$ ($\text{Ln} = \text{Sm-Lu}$, Y) have a facial octahedral geometry. Not only do we observe a reduction in the coordination number of the complexes by one, as is common as the lanthanide series is traversed [1-3], but, uniquely, for the metals at the centre of the lanthanide series ($\text{Sm} - \text{Tb}$) we observe that both seven and six coordinate complexes can be obtained from the appropriate synthetic routes suggesting a delicate energy balance between the two species.

Acknowledgements

We are grateful to the Engineering and Physical Sciences Research Council (UK) for a studentship to SS (EP/D072859/1) and for a Senior Fellowship to PRR (EP/D072859/1).

Conflict of Interests

The authors declare that they have no conflicts of interest.

Credit Author Statement

Lawrence Chan: Sample preparation and data analysis. **Simon A Cotton:** Conceptualization, supervision, validation, manuscript preparation. **Joanna Harris:** Sample preparation and data

- [14] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M.C. Burla, G. Polidori, M. Camalli, J. Appl. Crystallogr., 27 (1994) 435.
- [15] G. Sheldrick, Acta Crystallogr. Sect. A, 46 (1990) 467-473.
- [16] G.M. Sheldrick, SHELXS-97 and SHELXL-97, Program for Crystal Structure Solution and Refinement, in, University of Gottingen, Gottingen, 1997.
- [17] D.M. Adams, Metal-Ligand and Related Vibrations Edward Arnold, London, 1967.
- [18] C.E. Housecroft, A.G. Sharpe, Inorganic Chemistry, 5th ed., Pearson, Harlow, England, 2018.
- [19] S. Alvarez, P. Alemany, D. Casanova, J. Cirera, M. Llunell, Shape maps and polyhedral interconversion paths in transition metal chemistry, Coord. Chem. Rev., 249 (2005) 1693-1708.
- [20] M. Llunell, D. Casanova, J. Cirera, P. Alemany, S. Alvarez, SHAPE. Program for the Stereochemical Analysis of Molecular Fragments by Means of Continuous Shape Measure and Associated Tools, in, Universitat de Barcelona, Barcelona, 2013.
- [21] G. Depaoli, P. Ganis, P.L. Zanonato, G. Valle, Polyhedron, 12 (1993) 1933-1938.
- [22] G. Depaoli, P. Ganis, P.L. Zanonato, Polyhedron, 12 (1993) 671-676.
- [23] S.-H. Lin, Z.-C. Dong, J.-S. Huang, Q.-E. Zhang, J.-X. Lu, Acta Crystallographica Section C, 47 (1991) 426-427.
- [24] G.R. Willey, T.J. Woodman, M.G.B. Drew, Polyhedron, 16 (1997) 3385-3393.
- [25] M.C. Gallazzi, F. Bianchi, L. Depero, M. Zocchi, Polymer, 29 (1988) 1516-1521.
- [26] K. Izod, S.T. Liddle, W. Clegg, Inorg. Chem., 43 (2004) 214-218.
- [27] D. Barr, A. Brooker, M. Doyle, S. Drake, P. Raithby, R. Snaith, D. Wright, Angew. Chem.-Int. Edit. Engl., 29 (1990) 285-287.
- [28] J. Fawcett, A.W.G. Platt, D.R. Russell, Polyhedron, 21 (2002) 287-293.
- [29] Z. Olejnik, T. Lis, I. Ondrejovicova, Acta Crystallogr. Sect. C-Cryst. Struct. Commun., 51 (1995) 2246-2249.
- [30] M.J. Glazier, W. Levason, M.L. Matthews, P.L. Thornton, M. Webster, Inorg. Chim. Acta, 357 (2004) 1083-1091.
- [31] L. J. Radonovic, M.D. Glick, Journal of Inorganic & Nuclear Chemistry, 35 (1973) 2745-2752.
- [32] S. Petricek, A. Demsar, L. Golic, J. Kosmrlj, Polyhedron, 19 (2000) 199-204.
- [33] J.L. Atwood, K.D. Smith, J. Chem. Soc.-Dalton Trans., (1974) 921-923.
- [34] G.B. Deacon, T. Feng, P.C. Junk, B.W. Skelton, A.N. Sobolev, A.H. White, Aust. J. Chem., 51 (1998) 75-89.
- [35] G.B. Deacon, T.C. Feng, P.C. Junk, G. Meyer, N.M. Scott, B.W. Skelton, A.H. White, Aust. J. Chem., 53 (2000) 853-865.
- [36] R.D. Shannon, Acta Crystallogr. Sect. A, 32 (1976) 751-767.
- [37] D.L. Kepert, L.I. Semenova, A.N. Sobolev, A.H. White, Aust. J. Chem., 49 (1996) 1005-1008.
- [38] J. Albertsson, I. Elding, , Acta Cryst., B33 (1977) 1460-1469
- [39] T. Kurisaki, T. Yamaguchi, H. Wakita, J. Alloy. Compd., 192 (1993) 293-295.

