**Lanthanide tri- and tetrathionates and their complexes with triphenylphosphine oxide**

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**Abstract**

Lanthanide tri- and tetrathionate containing species have been prepared in solution by the reaction of potassium tri- and tetrathionate with lanthanide perchlorates. Unstable solid materials from these reactions have been examined by infrared spectroscopy and electrospray mass spectrometry (ESI MS). There was evidence of the formation of $S_3O_6^{2-}$ and $S_4O_6^{2-}$ coordination to lanthanide ions, but it was not possible to produce material suitable for single crystal x-ray studies. The reaction of ethanol solutions from $Ln(ClO_4)_3$ / $K_2S_nO_6$ (n = 3,4) with triphenylphosphine oxide yielded crystalline materials which have been characterised by infrared spectroscopy, electrospray mass spectrometry, elemental analysis and single crystal X-ray diffraction. The trithionate complexes $[Ln(S_3O_6)(Ph_3PO)_4]ClO_4.3H_2O$ (Ln = Nd, Tb) have been isolated. The tetrathionate / $Ph_3PO$ reaction gave rise to significant disproportionation giving a small quantity of $[Nd(S_4O_6)(Ph_3PO)_4(H_2O)]ClO_4$, a different isomer of $[Nd(S_3O_6)(Ph_3PO)_4H_2O]ClO_4$, neodymium sulfate and elemental sulfur. The crystal structures of the two isomers of $[Nd(S_3O_6)(Ph_3PO)_4H_2O]ClO_4$ and that of $[Nd(S_4O_6)(Ph_3PO)_4H_2O]ClO_4$ are reported. The structure of $[Er(H_2O)_5(Ph_3PO)_2].5Ph_3PO.3[ClO^-_4]$, formed during the attempted preparation of erbium trithionate complexes, is also described.

## 1. Introduction

Metal complexes involving di-, tri- and tetrathionate ions, ($S_nO_6^{2-}$, n = 2, 3, 4), are largely limited to their role as anions in cationic complexes. There are a considerable number of compounds

containing dithionate in which the $[S_2O_6]^{2-}$ ion acts as an uncoordinated counterion. The coordinated ion occurs less frequently, but has been reported as a monodentate ligand with copper(II) [1-4] and zinc(II) [5] in complexes with N-containing macrocycles. Bridging dithionate has also been reported, and is found mainly in the $\kappa^2$-$OO$' mode [3, 6-9] but also as bridging $\kappa^2$-$O^2$ [10], again coordinated to Cu(II). Structures where a higher polythionate ion is coordinated to a metal are limited to bridging $S_3O_6^{2-}$ in $[Na(18-C-6)]_2S_3O_6$ [11] and $[Cu(S_3O_6)(H_2O)_4]_n$ [12] , bridging $S_4O_6^{2-}$ in $Cu(1,10-phen)_2S_4O_6$[13], and bidentate $S_4O_6^{2-}$ in $Mn(bipy)_2S_4O_6$ [14] and in $M(4,4$' dimethyl-2,2'-bipy$)_2S_4O_6$ M = Zn, Cd [15].

We have previously reported the preparation and structures of some lanthanide dithionates which gave a polymeric structure for $Nd_2(S_2O_6)_3 \cdot 14H_2O$ and their triphenylphosphine oxide complexes $Nd_2(S_2O_6)_3(Ph_3PO)_4 \cdot 8H_2O$ [16] and $Pr_2(S_2O_6)_3(Ph_3PO)_6 \cdot 6H_2O$ [17]. Other than these dithionates, there are no reports of lanthanide polythionates ($^-O_3S(S)_nSO_3^-$) or their coordination complexes, and we report here our investigation into these under-represented compounds with the aim of obtaining materials suitable for structural determination.


## 2. Results and discussion

### 2.1 Attempted preparation of lanthanide trithionates and tetrathionates

The preparation of lanthanide trithionates and tetrathionates was attempted by metathesis between $Ln(ClO_4)_3$ (Ln = La, Pr, Nd, Tb, Er, Yb) and $K_2S_nO_6$ in aqueous solution followed by precipitation of the potassium salts with ethanol in which the lanthanide polythionate species appeared soluble. On addition of ethanol, the ethanolic solutions retained the characteristic colour of the lanthanide ion (Pr and Nd) while precipitated material was white, indicating that it contained little or no insoluble lanthanide compounds. Attempted crystallisation of these solutions by fractional crystallisation led to the isolation of small quantities of materials which were analysed by infrared spectroscopy. The infrared spectra showed, in addition to peaks due to coordinated water at 3300 and 1630 $cm^{-1}$ respectively, strong absorptions due to $SO_3$ or $ClO_4^-$ groups between 1110-1080 $cm^{-1}$, 1010-1005 $cm^{-1}$, 930 -920 $cm^{-1}$ and 835 – 830 $cm^{-1}$ for the trithionates and 1220, 1180, 1050 and

1010 cm$^{-1}$ for the tetrathionates. These absorption bands are shifted to lower wavenumber in comparison to those observed in $Na_2S_3O_6$ and $K_2S_4O_6$ (which have strong bands at 1251, 1213, 1066, 1024 cm$^{-1}$ and 1255, 1224, 1195, 1037 and 1012 cm$^{-1}$ respectively), indicating that both $S_3O_6^{2-}$ and $S_4O_6^{2-}$ are coordinated to the lanthanide ion.

Reactions with heavier lanthanides led to the isolation of materials whose infrared spectra indicated that they contained significant amounts of sulfate [18]. We attribute this to the decomposition of both trithionate and tetrathionate in mildly acidic aqueous solution, which is known to produce thiosulfate and sulfate [19].

Electrospray mass spectra were obtained from methanol solutions of the materials obtained from the Pr and Nd reactions. These ESI-MS spectra confirm the presence of both lanthanide ion and polythionate in the isolated materials. Details of the observed ions and their assignments are given in Table S1. The spectra show that $[LnO(H_2O)_n]^+$ and $[LnO(MeOH)_n]^+$ are the most abundant ions in the positive ion mode. This behaviour is typical of the behaviour of lanthanide complexes with weakly coordinating anions under electrospray conditions [20]. There are a series of low abundance ions containing the trithionate and tetrathionate ions corresponding to $[Ln(S_3O_6)(MeOH)_m(H_2O)_n]^+$ (m = 0-2, n = 1-4) and $[Ln(S_4O_6)(H_2O)_2]^+$ Ln = Nd . Similarly the negative ion spectra (Table S2) show peaks associated with the trithionate and tetrathionate ions $[S_3O_6(MeOH)_n]^{2-}$ and $[S_4O_6H]^-$ as the most abundant ions in the spectra, with lower abundance ions from $[Ln(S_3O_6)_2(MeOH)_m]^-$, $[Ln(S_3O_6)_2(H_2O)_n]^-$ (Ln = Pr, Nd) and $[Nd(S_4O_6)_2]^-$ and $[ClO_4]^-$. Assignments are based on the calculated m/z values and comparison of theoretical and observed isotope profiles An example is shown in Figure 1 for the $[Nd(S_3O_6)_2]^-$ ion.
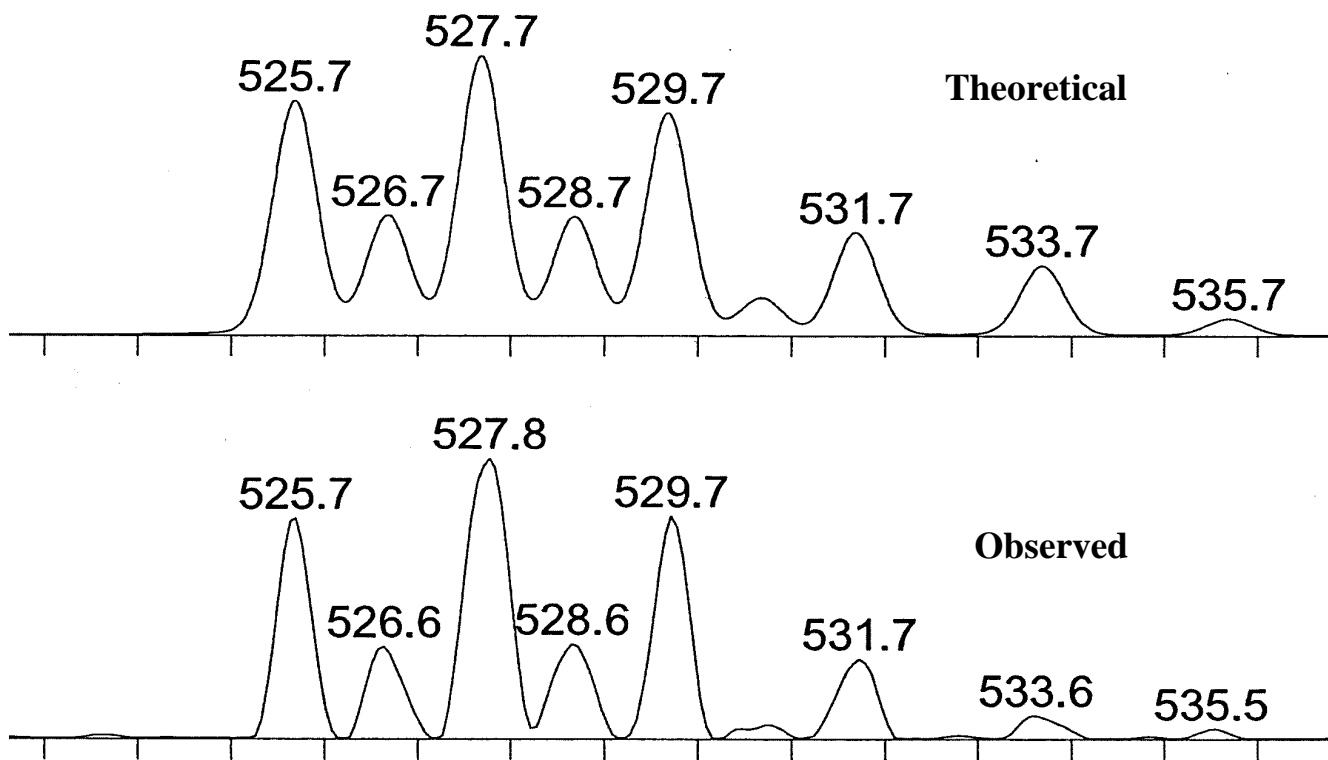
**Figure 1 Theoretical and Observed Isotope Profiles for [Nd(S$_3$O$_6$)$_2$]$^{2-}$**

Unfortunately, unlike the dithionates previously reported [16], and despite many attempts, it has proved impossible to produce crystalline material suitable for single crystal X-ray studies. From the available evidence (and see also below) it seems that full replacement of perchlorate by the polythionate ions has not occurred and the species produced are tentatively assigned as "[Ln(S$_n$O$_6$)(ClO$_4$)].xH$_2$O".

## 2.2 Coordination complexes of lanthanide trithionates with triphenylphosphine oxide

In view of the lack of success in preparing stable tri- and tetrathionates we attempted the *in situ* synthesis of coordination complexes in the hope that these might be more stable and give crystalline materials suitable for X-ray diffraction studies. Triphenylphosphine oxide often produces crystalline complexes with organic materials [21] and with lanthanide salts [22]. Thus, complex formation with Ph$_3$PO seemed a potential route to the synthesis of stable compounds which could be characterised by X-ray crystallography.

Ethanolic solutions of lanthanide trithionate species from the reaction of lanthanide perchlorates and the potassium trithionate, described above, were added to solutions of triphenylphosphine oxide. The bulk materials isolated by fractional crystallisation of the solutions gave elemental analyses which indicated that $[Ln(S_3O_6)(Ph_3PO)_4(H_2O)]ClO_4 \cdot 2H_2O$ could be produced up to Ln = Tb.

The infrared spectra of these materials are consistent with the formation of coordination complexes. The IR spectra show bands due to coordinated water, the P=O stretch at around 1140 $cm^{-1}$ , and a complex series of intense absorptions at around 1290, 1090, 1040 and 660 $cm^{-1}$ due to S-O and Cl-O stretches. The P=O stretch is significantly lower than observed in free $Ph_3PO$ (1190 $cm^{-1}$).

The isolated complexes are poorly soluble in most common organic solvents and it has not been possible to obtain NMR spectra in any organic solvent but methanol. The ^{31}P NMR spectra of methanolic solutions of the complexes showed a single signal close to that of free $Ph_3PO$. The absence of significant paramagnetic shifts indicates that in this solvent extensive dissociation occurs on dissolution.

Fractional crystallisation of the original ethanol solution of the Nd complex gave crystals suitable for X-ray diffraction studies. Full descriptions of the data collection and refinement are given in the supplementary information, as are figures of the structures with thermal ellipsoids at 50% probability together with full listings of bond distances and angles. The crystalline material was shown to be aqua trithionato-$\kappa^4 O,O,O',O'$ tetrakis-triphenylphosphine oxide neodymium(III) perchlorate. The cation, $[Nd(S_3O_6)(Ph_3PO)_4(H_2O)]^+$, is 9-coordinate: the neodymium ion is bound to the 4 oxygen atoms from the $Ph_3PO$ ligands, the oxygen atom of the water molecule, and 4 oxygen atoms from the trithionate ion (two from each $SO_3$ group),.

**Table 1 Selected bond distances[a] (Å) in $[Nd(S_3O_6)(Ph_3PO)_4(H_2O)]^+$**

| Bond | $Nd(S_3O_6)(Ph_3PO)_4(H_2O)]^+$ | | $K_2S_3O_6$[b] | (Na-18C-6)$_2$ - $\mu$- $S_3O_6$[c] | $[Cu(H_2O)_4\mu S_3O_6]_n$[d] |
|---|---|---|---|---|---|
| | $K^4$-O,O,O',O' | $K^3$-O,O, O'[e] | | | |
| $O_3$S-S | 2.10(2) | 2.11(4) | 2.083(22) | 2.111(8) | 2.132(18) |

| | | | | | |
|---|---|---|---|---|---|
| S-O(M) | 1.50(9) | 1.46(2) | | 1.445(2) | 1.452(3) |
| S=O | 1.43(3) | 1.40(3) | 1.450(6) | 1.440(4) | 1.450(4) |
| Nd-O(S) | 2.59(11) | 2.59(15) | | | |
| Nd-O(P) | 2.334(18) | 2.36(1) | | | |
| P=O | 1.504(1) | 1.504(5) | | | |
| Nd-O(H$_2$O) | 2.65(13) | 2.51(4) | | | |
| | | | | | |

a. Values in parenthesis are standard deviations which reflect the variation in bond distances rather than uncertainties in the data collection. b. data from ref 23 c. data from ref 14. d. data from ref 15 e. see below

The uncoordinated perchlorate ion is hydrogen bonded to the coordinated water by two oxygen atoms, the O…..O distances are 2.856 and 2.783 Å. The bond distances are summarised in Table 1 and compared with those of K$_2$S$_3$O$_6$ [23], the $\kappa^3$ complex discussed in section 2.3, and two other published trithionato-complexes.  The S-SO$_3$ distances do not differ significantly from the previously published structures, but the S=O bond is slightly shorter in the Nd complex.  The S-O(Nd) distance is significantly longer than the S=O length as expected on coordination to the more highly charged lanthanide ion.  The geometry of the cation was analysed using the SHAPE programme which locates the idealised structure which best conforms to the observed geometry [22, 23].  In this case two geometries give good descriptions of the structure, a 1,5,3 "muffin", and a capped square antiprism [24].  Both representations of the structure are shown in Figure 2.



**A**                                                                                    **B**
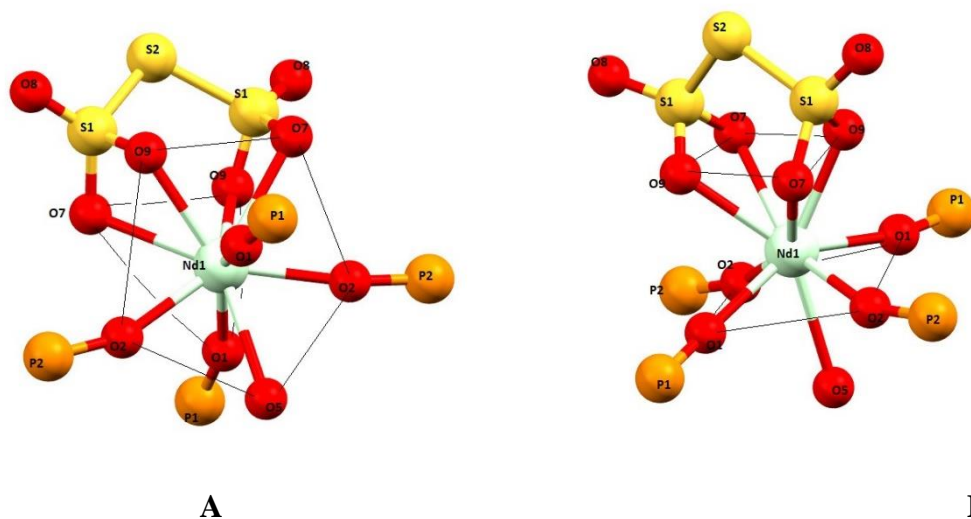
**Figure 2 The core structures of A. the "muffin" and B. the capped square antiprism views of *[κ⁴-O,O,O′,O′-* Nd(S₃O₆)(H₂O)(Ph₃PO)₄]⁺.  Hydrogen atoms, phenyl groups and perchlorate ions omitted for clarity.**

In the 1,5,3 "muffin" geometry O1 is the 1- atom, the 5-plane is defined by O2,O2,O5,O7 and O9 and the 3-plane by O1, O7 and O9.  The angle between the 5- and 3-planes is 14.3° and the deviation of the oxygen atoms in the 5-plane ranges between 0.006 – 0.320 Å.   In the square antiprismatic representation the square planes are defined by the O1, O1, O2, O2 from the $Ph_3PO$ and the O7, O7, O9 and O9 atoms from the trithionate.  The planes are parallel with the deviation of the oxygen atoms from the mean planes of 0.052 Å and 0.114 Å respectively.

The Nd and three sulfur atoms are coplanar with the coordinated oxygen atoms lying on average 1.03  Å above and below this plane, such that the 6-membered ring adopts a chair configuration.

Attempted preparation of the erbium trithionate - triphenylphosphine oxide complex led to a solid whose elemental analysis did not correspond to any simple trithionate complex. The absence of strong S-O stretches at around 1290 cm⁻¹ in the infrared spectrum of the isolated solid indicated that the trithionate ion was not present.   Small amounts of crystalline material were obtained which single crystal x-ray diffraction showed to be $[Er(H_2O)_5(Ph_3PO)_2]^.(Ph_3PO)_5^.3[ClO_4]$.  The structure is shown in Figure 3.  The erbium ion is 7-coordinate with a pentagonal bipyramidal geometry made up by 5 water molecules in the equatorial plane and 2 axial $Ph_3PO$ in the first coordination sphere. The remaining 5 $Ph_3PO$ molecules are H-bonded to the coordinated waters. The structure is similar to those of $[Ln(H_2O)_5(Cy_3PO)_2]^.2Cy_3PO^.[X]_3$ X = $CF_3SO_3$ [25], Cl [26, 27] and Br [26, 28]. The coordinated water molecules lie within 0.06 Å of the mean O8, O9, O10, O11, O12 plane. This is the first time this type of complex has been reported with a relatively smaller and lower basicity triaryl phosphine oxide.  The structure is unusual in that 5 $Ph_3PO$ are hydrogen bonded and presumably this is reflection of the lower steric demands of $Ph_3PO$ compared to $Cy_3PO$.
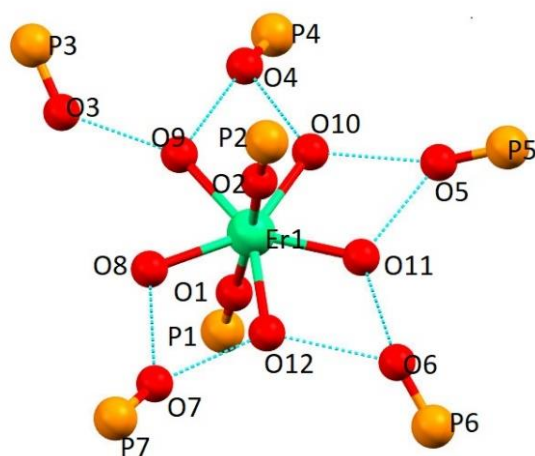
**Figure 3 The core structure of the [Er(H₂O)₅(Ph₃PO)₂·(Ph₃PO)₅]³⁺ cation. Blue broken linies represent hydrogen bonds. Hydrogen atoms, phenyl groups and perchlorate ions omitted for clarity**

## 2.3 Coordination complexes of lanthanide tetrathionates with triphenylphosphine oxide

Attempted preparation of triphenylphosphine oxide complexes of tetrathionates by the same method as the trithionates led to mixtures of compounds. The reaction of triphenylphosphine oxide with the ethanolic solutions obtained from the mixing of potassium tetrathionate and neodymium perchlorate was studied in detail. Four different solid products were identified from slow evaporation of the reaction mixture and a sample was mechanically separated into individual components. A small quantity of crystals formed at the air solution interface during slow evaporation of the solution which single crystal X-ray diffraction showed to be aqua tetrathionato-$\kappa^2$-*O,O′*-tetrakis-triphenylphosphine oxide neodymium(III) perchlorate, [Nd(S₄O₆)(Ph₃PO)₄(H₂O)]ClO₄. Electrospray mass spectrometry of this complex in methanol shows that extensive dissociation and ligand redistribution occurs under the experimental

conditions. Details of the ions identified are given in supplementary material in Table S3.

Filtration of the reduced solution produced larger quantities of a different crystalline complex, elemental sulfur and a lilac powder. The infrared spectrum of the crystalline material was very similar to that of the trithionate complex reported in section 2.2 and showed only slight differences in the positions of absorption maxima and their relative intensities. (See Figure S1 in the supplementary information). On analysis by single crystal x-ray diffraction this proved to be aqua trithionato-$\kappa^3 O,O,O'$ -tetrakis-triphenylphosphine oxide neodymium(III) perchlorate, $[Nd(S_3O_6)(Ph_3PO)_4(H_2O)]ClO_4$ (discussed below). The presence of elemental sulfur was confirmed by gas chromatography – mass spectrometry of a carbon disulfide solution which had an identical retention time and mass spectrum to that of an authentic sample of sulfur, m/z 256 with an isotope profile matching that of $S_8$. The lilac powder had an infrared spectrum which showed the presence of coordinated water but no triphenylphosphine oxide, and no bands in the 1200 cm$^{-1}$ region which could be associated with tri- or tetrathionate. Instead a series of 4 intense bands at 1101, 996, 934 and 752 cm$^{-1}$ were observed. The presence of 4 S-O stretches is expected for bridging sulfate and the spectra were similar to those reported for $Ln_2(SO_4)_3 \cdot 8H_2O$ [31, 32]. The presence of trithionate, elemental sulfur and sulfate indicates that a complex disproportionation reaction or series of reactions is occurring. The decomposition of tetrathionate to trithionate and thiosulfate under a variety of conditions has been reported [19] and the thiosulfate produced in these reactions could further decompose in mildly acidic solution to elemental sulfur and sulfur dioxide, although the latter was not detected in our system.

The cation in $[Nd(S_4O_6)(H_2O)(Ph_3PO)_4]ClO_4$ is 7-coordinate: the central Nd ion is bound to 2 oxygen atoms of the tetrathionate ligand (one from each $SO_3$ group), 4 oxygen atoms from the $Ph_3PO$ and the oxygen atom of the water molecule. Analysis of the geometry of the cation, as above, gives a bicapped trigonal prism as the best fit to common 7-coordinate structures [33]. The trigonal faces are defined by the O1, O2, and O4 atoms from the two phoshine oxides and the tetrathionate respectively. The angle between the triangular faces is 5.03°. The water oxygen atom,

O3, caps the O1,O1,O2,O2 square face.  The angle between the square faces ranges between 68.3 to 55.9° with an average of 60°. The core coordination in the complex cation is shown in Figure 4.
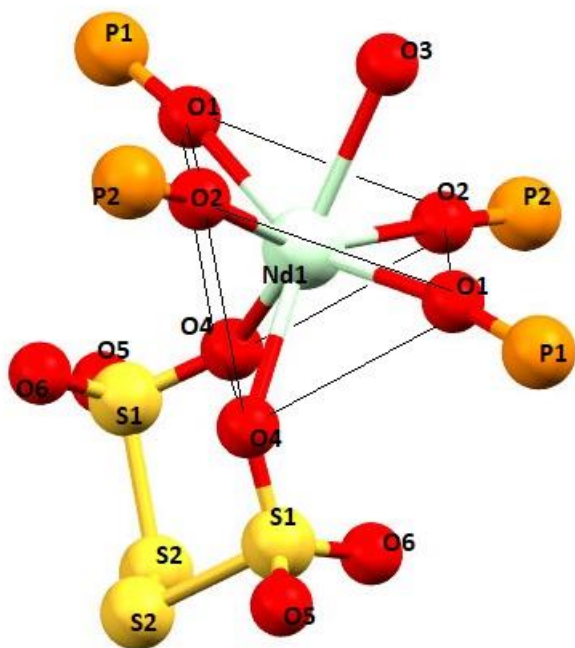


**Figure 4  The core structure of the capped trigonal prismatic  [Nd(S₄O₆)(H₂O)(Ph₃PO)₄]⁺.**

**Hydrogen atoms, phenyl groups and perchlorate ions omitted for clarity.**

In a similar manner to the trithionate analogue, the perchlorate ion is hydrogen bonded via two

oxygen atoms (O….O 2.868 Å) and this is reflected in a slight lengthening of the Cl-O bonds

(1.434 compared to 1.399 Å).  The bond distances are summarised in Table 2 and compared with

those found in $K_2S_4O_6$ [34] and complexes where the tetrathionate ion acts as a chelate [14, 15].

As observed for the trithionate complex, the $S-SO_3$ bond distances are little affected by

coordination to the neodymium compared to the tetrathionate ion in $K_2S_4O_6$ but are marginally

longer than in complexes with divalent metal ions. The bond distances within the coordinated

tetrathionate ion are little affected by binding to the metal in the Nd complex and those with Mn

[14], Zn and Cd [15].  The exception to this is the S-O(M) length which is significantly longer due

to coordination to the trivalent Nd centre.

**Table 2  Selected bond distances (Å) and angles(°) in [$k^2$-$O,O'$ Nd(S₄O₆)(H₂O)(Ph₃PO)₄]⁺**

**compared with known structures**

| | [Nd(S₄O₆)(H₂O)(Ph₃PO)₄]⁺ | $K_2S_4O_6$[b] | Mn(S₄O₆)(bipy)₂[c] | Zn(S₄O₆)L₂[d] | Cd(S₄O₆)L₂[d] |
|---|---|---|---|---|---|

| | | | | | |
|---|---|---|---|---|---|
| O$_3$S-S | 2.115(3)[a] | 2.117 | 2.066 | 2.106 | 2.101 |
| S-S | 2.011(4) | 2.017 | 1.963 | 2.016 | 2.017 |
| S-O(M) | 1.477(2) | 1.446 | 1.446 | 1.441 | 1.430 |
| S=O | 1.425(16) | 1.446 | 1.410 | 1.421 | 1.411 |
| M-O(S) | 2.431(20) | 2.89 | 2.122 | 2.277 | 2.120 |
| M-O(P) | 2.348(30) | | | | |
| P=O | 1.512(9) | | | | |
| M-O(H$_2$O) | 2.547(16) | | | | |
| (M)-O-S-S | 104.18 | | 107.13 | 107.26 | 107.56 |
| M-O-S | 133.00 | | 155.45 | 155.99 | 149.52 |
| O$_3$S-S-S | 104.41 | | 102.77 | 103.50 | 103.74 |
| O-M-O | 76.75 | | 93.33 | 93.27 | 94.03 |
| | | | | | |

a. Values in parenthesis are standard deviations which reflect the variation in bond distances rather than uncertainties in the data collection. b. data from ref 33, c. data from ref 14, d. data from ref 15 L = 4,4′-dimethyl-2,2′-bipy

The 7-membered S$_4$O$_2$Nd ring adopts a distorted twist chair conformation [35, 36] with the NdO$_2$ and the two S-atoms approximately planar, and the SO$_3$ sulfurs about 0.89 Å out of plane. In this the conformation differs from that found in other tetrathionate chelates which do not adopt any of the idealised conformations of the standard cycloheptane ring [35] and instead have a planar arrangement of the MO$_2$ and the SO$_3$ sulfur atoms with the remaining S-atoms between 0.67 to 0.88 Å above and below this plane.  The differences in the ring conformations are illustrated in Figure 5.   In the transition metal complexes the tetrathionate is relatively free from steric interactions with the remaining ligand set and the conformation is presumably that which the unconstrained tetrathionate adopts. There is considerably more steric congestion in the Nd complex as illustrated in Figure 5.  There are no strong interactions between the ring and the Ph$_3$PO ligands. The closest contacts which might be considered as H-bonding interactions are between O(11) and the H(48), H(62) and H(63)-atoms of the aromatic rings with an average O….H distance of 2.714 Å, but these values lie outside the sum of Van der Waals radii for O and H of 2.6 Å.
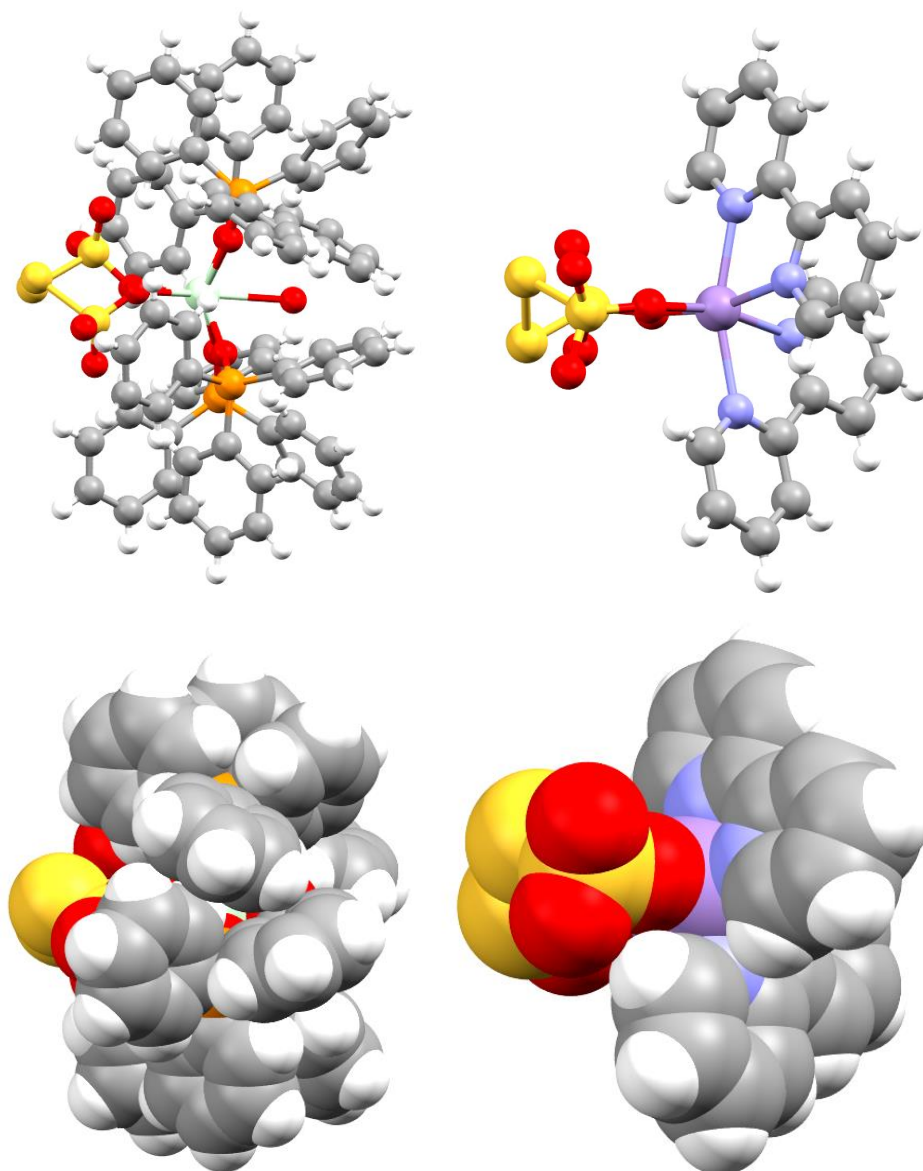
**Figure 5 The ring conformation of the tetrathionate in [Nd(S$_4$O$_6$)(Ph$_3$PO)(H$_2$O]$^+$ (left) and Mn(S$_4$O$_6$)(bipy)$_2$ (right, image generated using coordinates from ref 14) in ball and stick (upper) and space filling (lower) representations. Colour coding: sulfur – yellow, oxygen – red, carbon – grey, nitrogen – lilac, manganese – purple, phosphorus – orange, neodymium – pale green, hydrogen - white**

The trithionate complex formed from the tetrathionate reaction mixture differs from that produced by the direct trithionate reaction in that both the cations in the unit cell are 8- rather than 9- coordinate with the trithionate bonding in a $\kappa^3$-$O,O,O'$ mode. Full details of the data collection and refinement and full listings of bond distances and angles are given in the supplementary information. The bond distances are essentially the same as found for the $\kappa^4$ – coordination mode and the data are given in Table 1. The 8-coordinate cation adopts a bicapped trigonal prismatic

geometry which is illustrated for one of the molecules in the unit cell in Figure 6. The formation of

a different isomer in this reaction illustrates the high sensitivity of the final product to the exact

conditions during crystallisation and the relatively small energy difference between coordination

modes for lanthanide complexes.
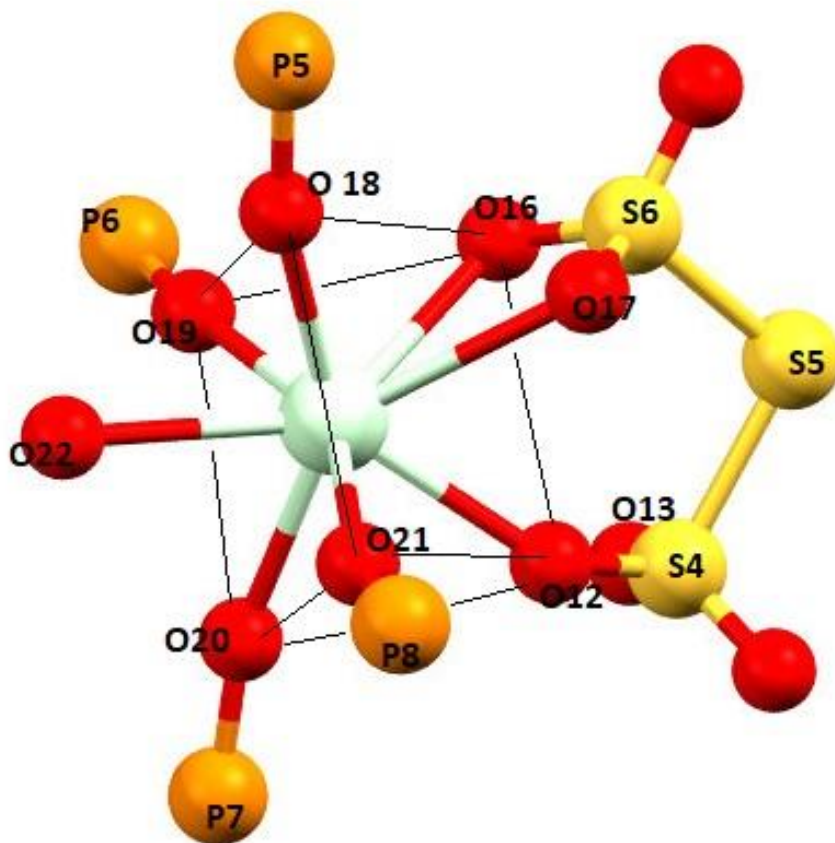


**Figure 6 The bicapped trigonal prismatic core geometry of $[Nd(S_3O_6)(Ph_3PO)_4(H_2O)][ClO_4]$. Hydrogen atoms, phenyl groups and perchlorate ions omitted for clarity.**

**Conclusion**

Lanthanide trithionates and tetrathionates have proved impossible to isolate as pure compounds.

Coordination complexes of lanthanide trithionates with triphenylphosphine oxide appear to be

stable for the lighter lanthanides. Whilst tetrathionate complexes with $Ph_3PO$ can be isolated in

small amounts, the predominant reaction appears to be a disproportionation leading to the isolation of a different isomer of the trithionate complex, sulfate and elemental sulfur.

**Experimental**

**Materials and methods**

Lanthanide perchlorates were prepared from the reaction of perchloric acid with a small excess of the lanthanide oxide.  Filtration followed by evaporation and drying in vacuo over KOH gave the hydrated perchlorates as crystalline solids.

Triphenylphosphine oxide, and potassium tetrathionate were commercial samples and used as received.  Potassium trithionate was prepared by the reaction of sodium thiosulphate with hydrogen peroxide and the potassium salt obtained by metathesis with aqueous solutions of sodium trithionate and potassium acetate [37].

 **[Nd(S₃O₆)(Ph₃PO)₄ (H₂O)]ClO₄·2H₂O**  A solution of Nd(ClO₄)₃ 0.99 g (2.8 mmol) in 1.5 mL and a slurry of  K₂S₃O₆ (0.97 g, 3.6 mmol in 3 mL H₂O) were and stirred at 0°C for 20 minutes. Ethanol (50 mL) was added and stirring continued for a further 30 minutes at 0°C.  The solution was filtered into a solution of triphenylphosphine oxide (1.99 g 7.2 mmol in 10 mL ethanol). During the addition the solution became cloudy and on standing a lilac powder together with more crystalline material formed.  This was filtered, washed with ethanol and dried at the pump to give 0.86 g (30% based on Ph₃PO).

Analysis for [Nd(S₃O₆)(Ph₃PO)₄]ClO₄·3H₂O  required(found)  C 53.94(53.69)  H 4.15(3.80)

Infrared spectrum (ATR)  3364 (br, w), 3061(w), 1591(w), 1486(w), 1436(s), 1288(m), 1143(s), 1119(s), 1087(s), 1042(s), 996(s), 922(w), 752(m), 722(s), 692(s), 655(m)

**[Tb(S₃O₆)(Ph₃PO)₄(H₂O)]ClO₄·2H₂O**  Using the method above Tb(ClO₄)₃  (0.89 g, 1.6 mmol in 2 mL water), K₂S₃O₆ (1.00 g, 3.7 mmol in  3mL water) and Ph₃PO (2.06 g 7.4 mmol in 25 mL)  gave a white powder on slow evaporation of the solution; 0.67 g (22% based on Ph₃PO).

Analysis for [Tb(S₃O₆)(Ph₃PO)₄(H₂O)]ClO₄·2H₂O required(found)  C 53.45(53.49)  H 4.11(3.77)

Infrared spectrum (ATR)  3350 (br, w), 3057(w), 1591(w), 1486(w), 1435(s), 1292(m), 1144(s), 1120(s), 1088(s), 1042(s), 996(s), 922(m), 750(m), 723(s), 689(s), 653(m)

**[NdS$_4$O$_6$(Ph$_3$PO)$_4$(H$_2$O)]ClO$_4$** The solution from Nd(ClO$_4$)$_3$ (0.98 g in 2 mL water) and K$_2$S$_4$O$_6$ (1.66 g, 5.4 mmol in 5.5 mL water) was filtered into a solution of triphenylphosphine oxide (1.84 g 2.8 mmol in 18 mL ethanol)  Crystals of [NdS$_4$O$_6$(Ph$_3$PO)$_4$(H$_2$O)]ClO$_4$ suitable for X-ray diffraction (<0.01 g) formed at the liquid / air interface during slow evaporation of the solution. Analysis [NdS$_4$O$_6$(Ph$_3$PO)$_4$(H$_2$O)]ClO$_4$ requires (found) C54.08(53.93) H3.91(3.81)  The bulk material, was isolated from the reduced solution by filtration as a lilac powder and mechanically separated into lilac blocks of [Nd(S$_3$O$_6$)(Ph$_3$PO)$_4$H$_2$O]ClO$_4$·2H$_2$O (0.16 g),  a microcrystalline lilac solid Nd$_2$(SO$_4$)$_3$·8H$_2$O (0.02 g), and elemental sulfur.

**Infrared spectra** were recorded with a resolution of ±1 cm$^{-1}$ on a Thermo Nicolet Avatar 370 FT-IR spectrometer operating in ATR mode.  The samples were compressed onto the optical window and spectra recorded without further sample pre-treatment.

**GC-Mass Spectrometry** was carried out on Perkin Elmer Clarus 500 by manual injection of 1 μL of a CS$_2$ solution onto a Supelco SLM- 5m fused silica column (30 m x 0.32 mm x 0.25 μm film thickness) using helium carrier gas (flow rate 1.5 mL min$^{-1}$).  The inlet temperature was 250$^{\circ}$C and the oven temperature programme 180$^{\circ}$C for 20 mins and increased at 15$^{\circ}$C min$^{-1}$ to 280$^{\circ}$C.  The mass spectrometer scanned between m/z 50-500.

**Electrospray mass spectra** were obtained by the EPSRC National Mass Spectrometry Service Centre at Swansea University. The spectra were recorded on a VG Quattro II triple quadrupole mass spectrometer. Samples dissolved in the appropriate solvent (water for lanthanide thoisulfates and polythionates, or CH$_2$Cl$_2$ for the triphenylphosphine oxide complexes) were loop injected into a stream of MeOH passing through a steel capillary held at high voltage (+3.5 kV for positive mode and −3.0 kV for negative mode). Nebulisation of the resulting spray was pneumatically assisted by a flow of nitrogen bath gas and heated source (70 °C). Declustering and molecular fragmentation were promoted by increasing the cone voltage from 8 to 50 V.

**X-Ray crystallography**

Full details of the data collection and refinement, together with ORTEP plots showing the thermal motion at 50% probability level are given in the supplementary information. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 1957467 for $[Er(Ph_3PO)_2(H_2O)_5]\cdot5(Ph_3PO)\cdot3[ClO_4]$, CCDC 1957468 for $[Nd(\kappa^4\text{-}O,O,O',O'\text{-}S_3O_6)(Ph_3PO)_4(H_2O)]\cdot3[ClO_4]$, CCDC 1957469 $[Nd(\kappa^2\text{-}O, O'\text{-} S_4O_6)(Ph_3PO)_4(H_2O)]\cdot3[ClO_4]$, and CCDC 1957470 $[Nd(\kappa^3\text{-}O,O,O'\text{-}S_3O_6)(Ph_3PO)_4(H_2O)]\cdot3[ClO_4]$ respectively. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: þ44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk

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# Supplementary Information

**Table S1 Electrospray mass spectra[a] of lanthanide tri- and tetrathionate species; positive ion mode**

| | $Ln_2(S_3O_6)_3$ | | | | | | $Ln_2(S_4O_6)_3$ | | |
|---|---|---|---|---|---|---|---|---|---|
| $[Ln(S_3O_6)(MeOH)_m(H_2O)_n]^+$ | | | | | | | $[Ln(S_4O_6)(MeOH)_m(H_2O)_n]^+$ | | |
| m = 0 | | | | | | | m = 0 | | |
| n | 0 | 1 | 2 | 3 | 4 | n | 1 | 2 | 3 |
| Pr | | | | | | | | | |
| Nd | | | 369.8[b] (369.8) | 387.9 (387.9) | 405.8 (405.8) | | 383.7 (383.8) | 401.7 (401.8) | 419.8 (419.8) |
| m = 1 | | | | | | | | | |
| Pr | | 382.8 (382.8) | 400.8 (400.8) | 418.8 (419.2) | 436.9 (436.9) | | | | |
| Nd | | 384.0 (383.8) | 401.9 (401.8) | 419.9 (419.9) | | | | | |
| m = 2 | | | | | | | | | |
| Pr | 396.8 (396.8) | 414.8 (414.9) | 432.8 (432.9) | | | | | | |
| Nd | | | | | | | | | |
| $[LnO(H_2O)_n]^+$ | | | | | | | | | |
| Pr | 156.8 (156.9) | 174.8 (174.9) | | | | | | | |
| Nd | 157.9 (157.9) | 175.7 (175.9) | 193.7 (193.9) | | | | | | |

| [LnO(MeOH)ₙ]⁺ | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Pr | | 188.8 (188.9) | 220.9 (221.0) | | | | | |
| Nd | | 189.7 (189.9) | | | | | | |

a. The most intense peak in the isotope profile is quoted.

b. m/z observed (calculated)

**Table S2 Electrospray mass spectra[a] of of lanthanide tri- and tetrathionate species; negative ion mode**

| $[Ln(S_3O_6)_2(H_2O)_n]^-$ | n | 0 | 1 | | | | |
|---|---|---|---|---|---|---|---|
| Pr | | 524.0[b] (524.7) | | | | | |
| Nd | | 527.8 (527.7) | 545.7 (545.7) | | | | |
| | | | | | | | |
| $[Ln(S_3O_6)_2(MeOH)_n]^-$ | n | 1 | 2 | 3 | 4 | 5 | |
| Pr | | 556.8 (556.7) | 588.7 (588.7) | 620.6 (620.8) | 652.6 (652.9) | 684.6 (684.8) | |
| Nd | | 557.7 (557.7) | 589.6 (589.7) | | | | |
| $[S_3O_6(MeOH)_m]^{2-}$ | | 111.9 (112.0) | 127.9 (128.0) | 143.8 (143.7) | 159.8 (160.0) | 175.8 (176.0) | |

a. The most intense peak in the isotope profile quoted for Nd containing ions

b. m/z observed (calculated)

**Figure S1  Comparative infrared spectra of [$\kappa^3$-*O,O,O'*-Nd(S$_3$O$_6$)(Ph$_3$PO)$_4$(H$_2$O)]ClO$_4$ (red) and [$\kappa^4$-*O,O,O',O'*- Nd(S$_3$O$_6$)(H$_2$O)(Ph$_3$PO)$_4$]ClO$_4$ (blue)**
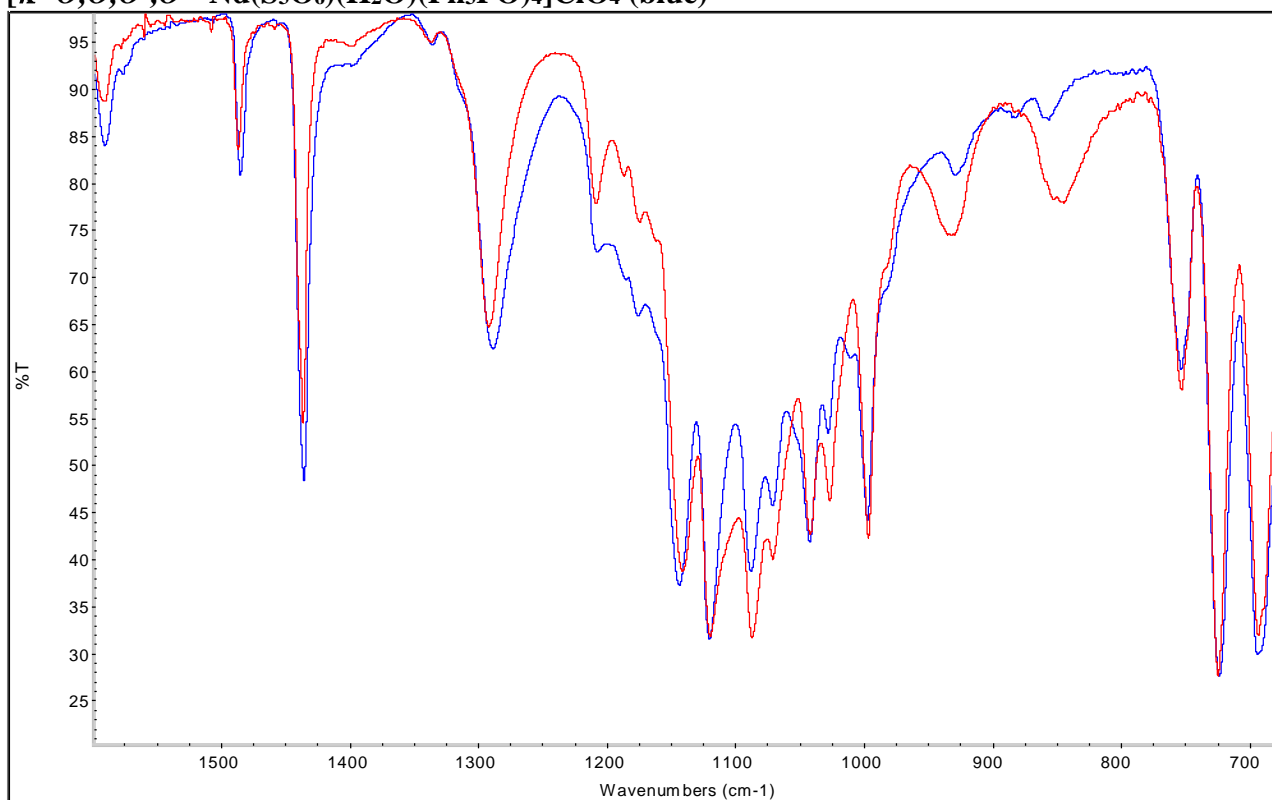
**Table S3 Electrospray mass spectra of [Ln(S$_4$O$_6$)(Ph$_3$PO)$_4$H$_2$O][ClO$_4$]**

| | [Ln(S$_4$O$_6$)(Ph$_3$PO)$_n$]$^+$ | | [Ln(Ph$_3$PO)$_n$ClO$_4$]$^{2+}$ | | [Ln(Ph$_3$PO)$_n$ClO$_4$]$^{2+}$ | |
| --- | --- | --- | --- | --- | --- | --- |
| Ln | Pr | Nd | Pr | Nd | Pr | Nd |
| 1 | | | | | | |
| 2 | | | | | 232.4(232.3) | 232.4(233.3) |
| 3 | 1199.3 (1199.0) | 1202.4(1202.0) | 537.3(537.0) | 538.8(538.5) | 325.2(325.0) | 326.0(326.0) |
| 4 | | | 676.3(676.0) | 677.7(677.5) | 418.0(417.7) | 418.9(418.7) |
| 5 | | | | | 510.8(510.3) | 511.5(511.3) |
| 6 | | | | | 603.5(603.3) | 604.4(604.0) |

# Crystal structures

# Crystal Data and Experimental [Nd($\kappa^4$-*O,O,O',O'*-$S_3O_6$)($Ph_3PO$)$_4$($H_2O$)]$\cdot$3[$ClO_4$]
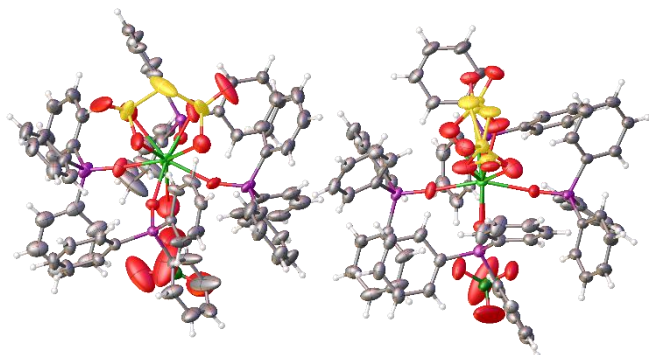


**Figure 1:** Thermal ellipsoids drawn at the 50% probability level.

**Experimental.** A suitable crystal of **ssf1275** (0.150×0.100×0.080 mm³) was selected and mounted on a suitable support on an Daresbury SRS station 9.8 diffractometer. The crystal was kept at a steady $T$ = 120(2) K during data collection. The structure was solved with the ShelXT (Sheldrick, 2015) structure solution program using the Intrinsic Phasing solution method and by using Olex2 (Dolomanov et al., 2009) as the graphical interface. The model was refined with version 2014/7 of ShelXL (Sheldrick, 2015) using Least Squares minimisation.

**Crystal Data.** $C_{72}H_{60}ClNdO_{15}P_4S_3$, $M_r$ = 1564.95, monoclinic, $C$2 (No. 5), a = 19.8173(9) Å, b = 17.2962(8) Å, c = 19.6261(9) Å, $\beta$ = 90.695(2)°, $\alpha$ = $\gamma$ = 90°, $V$ = 6726.6(5) Å³, $T$ = 120(2) K, $Z$ = 4, $Z'$ = 1, $\mu$ = 1.005 mm⁻¹, 33755 reflections measured, 18225 unique ($R_{int}$ = 0.0530) which were used in all calculations. The final $wR_2$ was 0.1630 (all data) and $R_1$ was 0.0614 (I > 2(I)).

| Formula | $C_{72}H_{60}ClNdO_{15}P_4S_3$ |
|---|---|
| $D_{calc.}$/ g cm⁻³ | 1.545 |
| $\mu$/mm⁻¹ | 1.005 |
| Formula Weight | 1564.95 |
| Colour | ? |
| Shape | ? |
| Size/mm³ | 0.150×0.100×0.080 |
| $T$/K | 120(2) |
| Crystal System | monoclinic |
| Flack Parameter | 0.479(13) |
| Hooft Parameter | 0.477(6) |
| Space Group | $C$2 |
| a/Å | 19.8173(9) |
| b/Å | 17.2962(8) |
| c/Å | 19.6261(9) |
| $\alpha$/° | 90 |
| $\beta$/° | 90.695(2) |
| $\gamma$/° | 90 |
| V/Å³ | 6726.6(5) |
| Z | 4 |
| Z' | 1 |
| Wavelength/Å | 0.6926 |
| Radiation type | Synchrotron |
| $\Theta_{min}$/° | 2.255 |
| $\Theta_{max}$/° | 29.672 |
| Measured Refl. | 33755 |
| Independent Refl. | 18225 |
| Reflections with I > 2(I) | 16848 |
| $R_{int}$ | 0.0530 |
| Parameters | 892 |
| Restraints | 808 |
| Largest Peak | 1.895 |
| Deepest Hole | -1.471 |
| GooF | 1.042 |
| $wR_2$ (all data) | 0.1630 |
| $wR_2$ | 0.1590 |
| $R_1$ (all data) | 0.0654 |
| $R_1$ | 0.0614 |

## Structure Quality Indicators

**Reflections:**

| d min (0.6926) | 0.70 | I/σ | 12.8 | Rint | 5.30% | complete | 97% |

**Refinement:**

| Shift | 0.000 | Max Peak | 1.9 | Min Peak | -1.5 | GooF | 1.042 |

A suitable crystal with dimensions 0.150×0.100×0.080 mm³ was mounted on a suitable support. Data were collected using the Daresbury SRS station 9.8 diffractometer, equipped with a Si(111) monochromator and Bruker SMART APEX2 CCD detector (Bruker, 2004), and operating at T = 120(2) K.

Data were measured using synchrotron radiation at a wavelength of 0.6911 Å. The maximum resolution that was achieved was $\Theta$ = 29.672° (0.70 Å).

The diffraction pattern was indexed using SAINT (Bruker, 2004).

Data reduction, scaling and absorption corrections were performed using Bruker SAINT. The final completeness is 98.30 % out to 29.672° in $\Theta$. An empirical absorption correction was performed using SADABS (Bruker, 2004). The absorption coefficient $\mu$ of this material is 1.005 mm⁻¹ at this wavelength ($\lambda$ = 0.6926 Å).

The structure was solved and the space group $C2$ (# 5) determined by the ShelXT (Sheldrick, 2015) structure solution program using Intrinsic Phasing and refined by Least Squares using version 2014/7 of ShelXL (Sheldrick, 2015). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. The Nd2 S3 bridge is disordered, and treated as disordered. The Nd1 S3 bride also seems disordered, but has not been treated as such.

There are 2 half molecules in the asymmetric unit, which is represented by the reported sum formula. In other words: Z is 4 and Z' is 1.

The Flack parameter was refined to 0.479(13). Determination of absolute structure using Bayesian statistics on Bijvoet differences using the Olex2 results in 0.477(6). Note: The Flack parameter is used to determine chirality of the crystal studied, the value should be near 0, a value of 1 means that the stereochemistry is wrong and the model should be inverted. A value of 0.5 means that the crystal consists of a racemic mixture of the two enantiomers. There is inverse twinning, approximately half-half.

## Reflection Statistics

| | | | |
|---|---|---|---|
| Total reflections (after filtering) | 33755 | Unique reflections | 18225 |
| Completeness | 0.886 | Mean I/$\sigma$ | 9.57 |
| $hkl_{max}$ collected | (27, 24, 27) | $hkl_{min}$ collected | (-27, -24, -27) |
| $hkl_{max}$ used | (27, 24, 27) | $hkl_{min}$ used | (-27, -24, 0) |
| Lim $d_{max}$ collected | 100.0 | Lim $d_{min}$ collected | 0.35 |
| $d_{max}$ used | 8.8 | $d_{min}$ used | 0.7 |
| Friedel pairs | 12302 | Friedel pairs merged | 0 |
| Inconsistent equivalents | 0 | $R_{int}$ | 0.053 |
| $R_{sigma}$ | 0.0782 | Intensity transformed | 0 |
| Omitted reflections | 0 | Omitted by user (OMIT hkl) | 0 |
| Multiplicity | (28151, 2661, 94) | Maximum multiplicity | 5 |
| Removed systematic absences | 0 | Filtered off (Shel/OMIT) | 0 |

**Table 1**: Bond Lengths in Å.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|------|------|----------|------|------|----------|
| Nd1 | O1¹ | 2.349(5) | O11 | S5² | 1.529(8) |
| Nd1 | O1 | 2.349(5) | O12A | S5² | 1.473(13) |
| Nd1 | O2 | 2.311(5) | O13 | O13¹ | 1.76(4) |
| Nd1 | O2¹ | 2.311(5) | C1 | C2 | 1.370(9) |
| Nd1 | O5 | 2.743(15) | C1 | C6 | 1.389(10) |
| Nd1 | O7¹ | 2.686(10) | C2 | C3 | 1.397(10) |
| Nd1 | O7 | 2.686(10) | C3 | C4 | 1.350(12) |
| Nd1 | O9¹ | 2.499(8) | C4 | C5 | 1.361(12) |
| Nd1 | O9 | 2.499(8) | C5 | C6 | 1.388(11) |
| Nd2 | S3² | 3.237(4) | C7 | C8 | 1.423(12) |
| Nd2 | S3 | 3.237(4) | C7 | C12 | 1.325(13) |
| Nd2 | O3 | 2.330(5) | C8 | C9 | 1.389(13) |
| Nd2 | O3² | 2.330(5) | C9 | C10 | 1.388(19) |
| Nd2 | O4² | 2.362(5) | C10 | C11 | 1.32(2) |
| Nd2 | O4 | 2.362(5) | C11 | C12 | 1.424(16) |
| Nd2 | O6 | 2.550(7) | C13 | C14 | 1.398(9) |
| Nd2 | O10 | 2.654(9) | C13 | C18 | 1.391(9) |
| Nd2 | O10² | 2.654(9) | C14 | C15 | 1.400(9) |
| Nd2 | O11² | 2.550(8) | C15 | C16 | 1.389(12) |
| Nd2 | O11 | 2.550(8) | C16 | C17 | 1.376(11) |
| Cl1 | O13¹ | 1.363(16) | C17 | C18 | 1.405(9) |
| Cl1 | O13 | 1.363(16) | C19 | C20 | 1.389(12) |
| Cl1 | O14 | 1.471(17) | C19 | C24 | 1.435(15) |
| Cl1 | O14¹ | 1.471(17) | C20 | C21 | 1.404(14) |
| Cl2 | O15² | 1.423(7) | C21 | C22 | 1.382(17) |
| Cl2 | O15 | 1.423(7) | C22 | C23 | 1.413(16) |
| Cl2 | O16² | 1.364(13) | C23 | C24 | 1.346(15) |
| Cl2 | O16 | 1.364(13) | C25 | C26 | 1.399(10) |
| S5 | S4² | 2.118(7) | C25 | C30 | 1.397(12) |
| S5 | S4 | 1.558(6) | C26 | C27 | 1.396(11) |
| S5 | O10² | 1.955(11) | C27 | C28 | 1.382(13) |
| S5 | O11² | 1.529(8) | C28 | C29 | 1.419(14) |
| S5 | O12A² | 1.473(13) | C29 | C30 | 1.382(12) |
| S2 | S1¹ | 2.079(4) | C31 | C32 | 1.377(10) |
| S2 | S1 | 2.079(4) | C31 | C36 | 1.394(11) |
| S4 | S5² | 2.118(7) | C32 | C33 | 1.396(14) |
| S4 | S4² | 1.138(11) | C33 | C34 | 1.349(17) |
| S1 | O7 | 1.578(10) | C34 | C35 | 1.392(14) |
| S1 | O8 | 1.403(8) | C35 | C36 | 1.381(13) |
| S1 | O9 | 1.425(8) | C37 | C38 | 1.395(9) |
| S3 | O10 | 1.439(11) | C37 | C42 | 1.402(9) |
| S3 | O11 | 1.277(9) | C38 | C39 | 1.395(9) |
| S3 | O12 | 1.425(12) | C39 | C40 | 1.386(12) |
| P1 | O1 | 1.507(5) | C40 | C41 | 1.418(13) |
| P1 | C1 | 1.805(6) | C41 | C42 | 1.367(10) |
| P1 | C7 | 1.785(7) | C43 | C44 | 1.399(11) |
| P1 | C13 | 1.795(6) | C43 | C48 | 1.388(10) |
| P2 | O2 | 1.510(6) | C44 | C45 | 1.381(11) |
| P2 | C19 | 1.772(9) | C45 | C46 | 1.378(12) |
| P2 | C25 | 1.801(8) | C46 | C47 | 1.381(12) |
| P2 | C31 | 1.775(8) | C47 | C48 | 1.392(10) |
| P3 | O3 | 1.503(5) | C49 | C50 | 1.396(11) |
| P3 | C37 | 1.794(6) | C49 | C54 | 1.398(10) |
| P3 | C43 | 1.806(7) | C50 | C51 | 1.395(11) |
| P3 | C49 | 1.784(8) | C51 | C52 | 1.392(12) |
| P4 | O4 | 1.504(5) | C52 | C53 | 1.373(15) |
| P4 | C55 | 1.793(7) | C53 | C54 | 1.377(13) |
| P4 | C61 | 1.793(7) | C55 | C56 | 1.404(11) |
| P4 | C67 | 1.804(7) | C55 | C60 | 1.380(10) |
| O10 | S5² | 1.955(11) | C56 | C57 | 1.376(11) |

| Atom | Atom | Length/Å | | Atom | Atom | Length/Å |
|------|------|----------|---|------|------|----------|
| C57 | C58 | 1.383(14) | | C67 | C68 | 1.382(10) |
| C58 | C59 | 1.373(13) | | C67 | C72 | 1.423(9) |
| C59 | C60 | 1.384(10) | | C68 | C69 | 1.394(10) |
| C61 | C62 | 1.419(11) | | C69 | C70 | 1.395(12) |
| C61 | C66 | 1.380(10) | | C70 | C71 | 1.371(13) |
| C62 | C63 | 1.384(12) | | C71 | C72 | 1.390(10) |
| C63 | C64 | 1.375(14) | | ---- | | |
| C64 | C65 | 1.409(14) | | | | |
| C65 | C66 | 1.372(10) | | | | |

[1]1-x,+y,-z; [2]2-x,+y,1-z

**Table2**: Bond Angles in °.

| Atom | Atom | Atom | Angle/° |
|------|------|------|---------|
| O1 | Nd1 | O1[1] | 146.7(3) |
| O1[1] | Nd1 | O5 | 73.35(13) |
| O1 | Nd1 | O5 | 73.35(13) |
| O1 | Nd1 | O7[1] | 115.0(2) |
| O1[1] | Nd1 | O7[1] | 88.5(2) |
| O1[1] | Nd1 | O7 | 115.0(2) |
| O1 | Nd1 | O7 | 88.5(2) |
| O1 | Nd1 | O9[1] | 75.2(2) |
| O1 | Nd1 | O9 | 134.8(2) |
| O1[1] | Nd1 | O9[1] | 134.8(2) |
| O1[1] | Nd1 | O9 | 75.2(2) |
| O2[1] | Nd1 | O1[1] | 83.8(2) |
| O2 | Nd1 | O1 | 83.8(2) |
| O2[1] | Nd1 | O1 | 83.3(2) |
| O2 | Nd1 | O1[1] | 83.3(2) |
| O2[1] | Nd1 | O2 | 134.1(3) |
| O2[1] | Nd1 | O5 | 67.03(15) |
| O2 | Nd1 | O5 | 67.03(15) |
| O2 | Nd1 | O7 | 154.1(2) |
| O2[1] | Nd1 | O7[1] | 154.1(2) |
| O2[1] | Nd1 | O7 | 69.0(3) |
| O2 | Nd1 | O7[1] | 68.9(3) |
| O2 | Nd1 | O9 | 129.7(3) |
| O2[1] | Nd1 | O9[1] | 129.7(3) |
| O2 | Nd1 | O9[1] | 88.5(2) |
| O2[1] | Nd1 | O9 | 88.5(2) |
| O7 | Nd1 | O5 | 133.8(2) |
| O7[1] | Nd1 | O5 | 133.8(2) |
| O7 | Nd1 | O7[1] | 92.4(4) |
| O9 | Nd1 | O5 | 141.74(18) |
| O9[1] | Nd1 | O5 | 141.74(18) |
| O9[1] | Nd1 | O7 | 65.6(3) |
| O9[1] | Nd1 | O7[1] | 47.6(3) |
| O9 | Nd1 | O7 | 47.6(3) |
| O9 | Nd1 | O7[1] | 65.6(3) |
| O9[1] | Nd1 | O9 | 76.5(4) |
| S3[2] | Nd2 | S3 | 63.86(15) |
| O3[2] | Nd2 | S3 | 108.40(15) |
| O3[2] | Nd2 | S3[2] | 95.26(17) |
| O3 | Nd2 | S3[2] | 108.40(15) |
| O3 | Nd2 | S3 | 95.26(17) |
| O3 | Nd2 | O3[2] | 152.2(3) |
| O3 | Nd2 | O4 | 85.92(19) |
| O3[2] | Nd2 | O4 | 86.4(2) |
| O3[2] | Nd2 | O4[2] | 85.93(19) |
| O3 | Nd2 | O4[2] | 86.4(2) |
| O3 | Nd2 | O6 | 76.11(14) |
| O3[2] | Nd2 | O6 | 76.11(14) |
| O3 | Nd2 | O10 | 69.4(3) |
| O3[2] | Nd2 | O10 | 133.6(2) |
| O3 | Nd2 | O10[2] | 133.6(2) |
| O3[2] | Nd2 | O10[2] | 69.4(3) |
| O3[2] | Nd2 | O11[2] | 116.1(3) |
| O3 | Nd2 | O11 | 116.1(3) |
| O3 | Nd2 | O11[2] | 86.8(3) |
| O3[2] | Nd2 | O11 | 86.8(3) |
| O4 | Nd2 | S3[2] | 137.04(14) |
| O4[2] | Nd2 | S3 | 137.04(14) |
| O4 | Nd2 | S3 | 74.87(14) |
| O4[2] | Nd2 | S3[2] | 74.87(14) |

| Atom | Atom | Atom | Angle/° |
|------|------|------|---------|
| O4 | Nd2 | O4[2] | 147.8(2) |
| O4 | Nd2 | O6 | 73.90(12) |
| O4[2] | Nd2 | O6 | 73.90(12) |
| O4 | Nd2 | O10[2] | 130.2(2) |
| O4 | Nd2 | O10 | 75.2(3) |
| O4[2] | Nd2 | O10[2] | 75.2(3) |
| O4[2] | Nd2 | O10 | 130.2(2) |
| O4[2] | Nd2 | O11[2] | 72.7(2) |
| O4[2] | Nd2 | O11 | 137.8(2) |
| O4 | Nd2 | O11 | 72.7(2) |
| O4 | Nd2 | O11[2] | 137.8(2) |
| O6 | Nd2 | S3 | 148.07(7) |
| O6 | Nd2 | S3[2] | 148.07(8) |
| O6 | Nd2 | O10 | 134.7(2) |
| O6 | Nd2 | O10[2] | 134.7(2) |
| O10[2] | Nd2 | S3[2] | 25.9(2) |
| O10 | Nd2 | S3[2] | 72.9(2) |
| O10[2] | Nd2 | S3 | 72.9(2) |
| O10 | Nd2 | S3 | 25.9(2) |
| O10[2] | Nd2 | O10 | 90.7(5) |
| O11 | Nd2 | S3 | 21.6(2) |
| O11[2] | Nd2 | S3[2] | 21.6(2) |
| O11[2] | Nd2 | S3 | 64.55(19) |
| O11 | Nd2 | S3[2] | 64.54(19) |
| O11[2] | Nd2 | O6 | 143.23(19) |
| O11 | Nd2 | O6 | 143.23(19) |
| O11[2] | Nd2 | O10[2] | 47.3(3) |
| O11 | Nd2 | O10[2] | 63.4(3) |
| O11[2] | Nd2 | O10 | 63.4(3) |
| O11 | Nd2 | O10 | 47.3(3) |
| O11[2] | Nd2 | O11 | 73.5(4) |
| O13[1] | Cl1 | O13 | 81(2) |
| O13[1] | Cl1 | O14 | 110.7(11) |
| O13 | Cl1 | O14 | 102.3(11) |
| O13 | Cl1 | O14[1] | 110.7(11) |
| O13[1] | Cl1 | O14[1] | 102.3(11) |
| O14 | Cl1 | O14[1] | 136.4(18) |
| O15[2] | Cl2 | O15 | 108.1(7) |
| O16[2] | Cl2 | O15 | 118.2(12) |
| O16[2] | Cl2 | O15[2] | 102.2(7) |
| O16 | Cl2 | O15[2] | 118.2(12) |
| O16 | Cl2 | O15 | 102.2(7) |
| O16[2] | Cl2 | O16 | 109(2) |
| S4 | S5 | S4[2] | 31.6(4) |
| S4 | S5 | O10[2] | 105.2(4) |
| O10[2] | S5 | S4[2] | 117.1(4) |
| O11[2] | S5 | S4[2] | 101.3(4) |
| O11[2] | S5 | S4 | 127.8(4) |
| O11[2] | S5 | O10[2] | 72.5(5) |
| O12A[2] | S5 | S4[2] | 99.6(7) |
| O12A[2] | S5 | S4 | 104.9(7) |
| O12A[2] | S5 | O10[2] | 143.1(8) |
| O12A[2] | S5 | O11[2] | 104.5(7) |
| S1 | S2 | S1[1] | 101.9(2) |
| S5 | S4 | S5[2] | 104.7(3) |
| S4[2] | S4 | S5[2] | 45.9(3) |
| S4[2] | S4 | S5 | 102.5(5) |
| O7 | S1 | S2 | 114.9(3) |
| O8 | S1 | S2 | 107.4(6) |
| O8 | S1 | O7 | 125.7(7) |

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|------|------|------|---------|------|------|------|---------|
| O8 | S1 | O9 | 113.5(5) | C18 | C13 | C14 | 119.1(6) |
| O9 | S1 | S2 | 103.4(3) | C13 | C14 | C15 | 120.2(7) |
| O9 | S1 | O7 | 88.5(6) | C16 | C15 | C14 | 120.2(7) |
| O10 | S3 | Nd2 | 53.8(4) | C17 | C16 | C15 | 119.8(7) |
| O11 | S3 | Nd2 | 47.3(4) | C16 | C17 | C18 | 120.4(7) |
| O11 | S3 | O10 | 100.3(6) | C13 | C18 | C17 | 120.3(6) |
| O11 | S3 | O12 | 124.6(7) | C20 | C19 | P2 | 120.6(9) |
| O12 | S3 | Nd2 | 150.6(5) | C20 | C19 | C24 | 118.2(9) |
| O12 | S3 | O10 | 117.5(7) | C24 | C19 | P2 | 121.2(7) |
| O1 | P1 | C1 | 110.5(3) | C19 | C20 | C21 | 121.1(11) |
| O1 | P1 | C7 | 109.6(3) | C22 | C21 | C20 | 119.7(10) |
| O1 | P1 | C13 | 112.4(3) | C21 | C22 | C23 | 119.3(11) |
| C7 | P1 | C1 | 109.2(3) | C24 | C23 | C22 | 121.4(13) |
| C7 | P1 | C13 | 107.4(3) | C23 | C24 | C19 | 120.2(11) |
| C13 | P1 | C1 | 107.6(3) | C26 | C25 | P2 | 122.2(6) |
| O2 | P2 | C19 | 110.8(4) | C30 | C25 | P2 | 118.2(6) |
| O2 | P2 | C25 | 110.0(4) | C30 | C25 | C26 | 119.6(7) |
| O2 | P2 | C31 | 112.6(3) | C27 | C26 | C25 | 119.6(8) |
| C19 | P2 | C25 | 108.7(4) | C28 | C27 | C26 | 121.2(8) |
| C19 | P2 | C31 | 105.9(4) | C27 | C28 | C29 | 119.0(8) |
| C31 | P2 | C25 | 108.7(4) | C30 | C29 | C28 | 119.9(9) |
| O3 | P3 | C37 | 112.7(3) | C29 | C30 | C25 | 120.7(8) |
| O3 | P3 | C43 | 110.3(3) | C32 | C31 | P2 | 123.3(7) |
| O3 | P3 | C49 | 111.1(3) | C32 | C31 | C36 | 118.0(8) |
| C37 | P3 | C43 | 109.1(3) | C36 | C31 | P2 | 118.7(6) |
| C49 | P3 | C37 | 106.3(3) | C31 | C32 | C33 | 120.6(10) |
| C49 | P3 | C43 | 107.1(3) | C34 | C33 | C32 | 120.5(9) |
| O4 | P4 | C55 | 113.2(3) | C33 | C34 | C35 | 120.3(10) |
| O4 | P4 | C61 | 110.3(3) | C36 | C35 | C34 | 118.9(10) |
| O4 | P4 | C67 | 111.1(3) | C35 | C36 | C31 | 121.6(9) |
| C55 | P4 | C61 | 105.9(3) | C38 | C37 | P3 | 121.9(5) |
| C55 | P4 | C67 | 108.2(3) | C38 | C37 | C42 | 120.0(6) |
| C61 | P4 | C67 | 107.8(3) | C42 | C37 | P3 | 118.1(5) |
| P1 | O1 | Nd1 | 163.0(3) | C37 | C38 | C39 | 119.3(7) |
| P2 | O2 | Nd1 | 158.8(4) | C40 | C39 | C38 | 121.1(8) |
| P3 | O3 | Nd2 | 174.0(4) | C39 | C40 | C41 | 118.9(7) |
| P4 | O4 | Nd2 | 166.9(3) | C42 | C41 | C40 | 120.3(7) |
| S1 | O7 | Nd1 | 101.4(4) | C41 | C42 | C37 | 120.5(7) |
| S1 | O9 | Nd1 | 115.9(6) | C44 | C43 | P3 | 118.4(5) |
| S5[2] | O10 | Nd2 | 103.5(4) | C48 | C43 | P3 | 121.9(5) |
| S3 | O10 | Nd2 | 100.3(5) | C48 | C43 | C44 | 119.7(6) |
| S5[2] | O11 | Nd2 | 124.8(6) | C45 | C44 | C43 | 119.6(7) |
| S3 | O11 | Nd2 | 111.1(6) | C46 | C45 | C44 | 120.8(8) |
| Cl1 | O13 | O13[1] | 49.7(10) | C45 | C46 | C47 | 119.9(7) |
| C2 | C1 | P1 | 118.6(5) | C46 | C47 | C48 | 120.3(7) |
| C2 | C1 | C6 | 118.6(6) | C43 | C48 | C47 | 119.8(7) |
| C6 | C1 | P1 | 122.7(5) | C50 | C49 | P3 | 122.8(5) |
| C1 | C2 | C3 | 119.9(7) | C50 | C49 | C54 | 118.7(7) |
| C4 | C3 | C2 | 121.0(7) | C54 | C49 | P3 | 118.4(6) |
| C3 | C4 | C5 | 119.8(7) | C51 | C50 | C49 | 121.0(7) |
| C4 | C5 | C6 | 120.3(8) | C52 | C51 | C50 | 118.5(9) |
| C5 | C6 | C1 | 120.3(7) | C53 | C52 | C51 | 120.9(9) |
| C8 | C7 | P1 | 120.2(6) | C52 | C53 | C54 | 120.6(8) |
| C12 | C7 | P1 | 120.1(7) | C53 | C54 | C49 | 120.2(9) |
| C12 | C7 | C8 | 119.4(8) | C56 | C55 | P4 | 121.2(6) |
| C9 | C8 | C7 | 118.6(10) | C60 | C55 | P4 | 119.9(6) |
| C10 | C9 | C8 | 120.6(11) | C60 | C55 | C56 | 118.8(7) |
| C11 | C10 | C9 | 118.5(10) | C57 | C56 | C55 | 119.4(9) |
| C10 | C11 | C12 | 122.5(13) | C56 | C57 | C58 | 121.1(9) |
| C7 | C12 | C11 | 119.1(12) | C59 | C58 | C57 | 119.8(8) |
| C14 | C13 | P1 | 118.3(5) | C58 | C59 | C60 | 119.7(8) |
| C18 | C13 | P1 | 122.2(5) | C55 | C60 | C59 | 121.2(7) |

| Atom | Atom | Atom | Angle/° |
|------|------|------|---------|
| C62 | C61 | P4 | 122.3(6) |
| C66 | C61 | P4 | 118.1(6) |
| C66 | C61 | C62 | 119.6(7) |
| C63 | C62 | C61 | 119.2(8) |
| C64 | C63 | C62 | 120.9(8) |
| C63 | C64 | C65 | 119.7(8) |
| C66 | C65 | C64 | 119.9(8) |
| C65 | C66 | C61 | 120.8(8) |
| C68 | C67 | P4 | 122.9(5) |

| Atom | Atom | Atom | Angle/° |
|------|------|------|---------|
| C68 | C67 | C72 | 120.6(6) |
| C72 | C67 | P4 | 116.5(5) |
| C67 | C68 | C69 | 119.6(7) |
| C68 | C69 | C70 | 119.9(8) |
| C71 | C70 | C69 | 120.5(7) |
| C70 | C71 | C72 | 121.0(7) |
| C71 | C72 | C67 | 118.3(7) |

————

[1]1-x,+y,-z; [2]2-x,+y,1-z
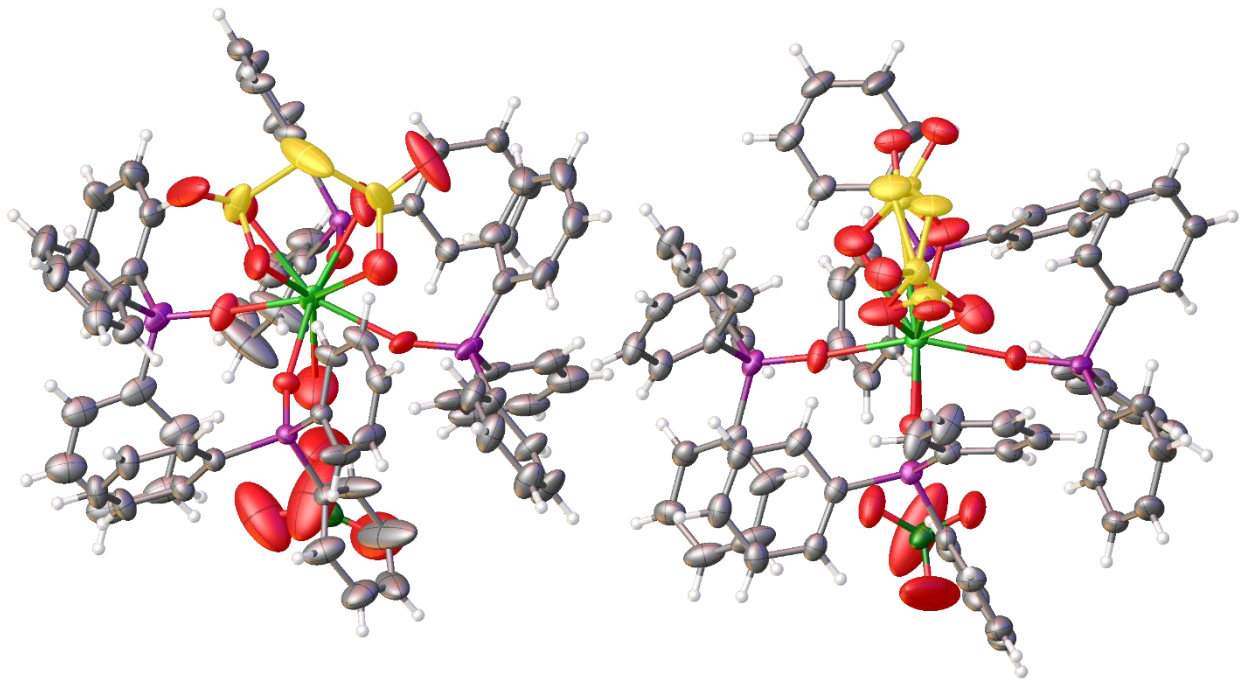
# Crystal Data and Experimental $[Nd(\kappa^2\text{-}O, O'\text{-} S_4O_6)(Ph_3PO)_4(H_2O)]\cdot 3[ClO_4]$
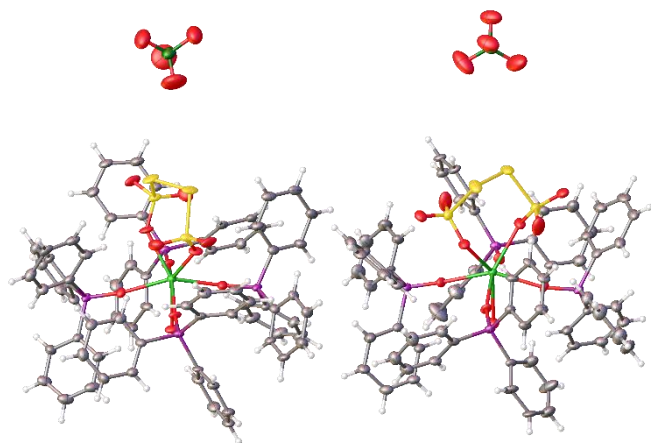


**Figure 1:** Thermal ellipsoids drawn at the 50% probability level.

**Experimental.** A suitable colourless cut shard-shaped crystal (0.220×0.140×0.090 mm³) was selected and mounted on a MITIGEN holder in perfluoroether oil on a Bruker-Nonius FR591 diffractometer equipped with a rotating anode and graphite monochromator and a Bruker-Nonius 95mm CCD camera on κ-goniostat. The crystal was kept at a steady $T$ = 120(2) K during data collection. The structure was solved with the **ShelXT** (Sheldrick, 2015) structure solution program using the Intrinsic Phasing solution method and by using **Olex2** (Dolomanov et al., 2009) as the graphical interface. The model was refined with version 2014/7 of **ShelXL** (Sheldrick, 2015) using Least Squares minimisation.

**Crystal Data.** $C_{72}H_{60}ClNdO_{15}P_4S_4$, $M_r$ = 1597.01, monoclinic, $C2$ (No. 5), a = 20.0936(7) Å, b = 17.3394(7) Å, c = 19.6719(7) Å, $\beta$ = 90.081(3)°, $\alpha$ = $\gamma$ = 90°, $V$ = 6853.9(4) Å³, $T$ = 120(2) K, $Z$ = 4, $Z'$ = 1, $\mu$(MoK$_\alpha$) = 1.080 mm⁻¹, 35506 reflections measured, 15571 unique ($R_{int}$ = 0.0770) which were used in all calculations. The final $wR_2$ was 0.2016 (all data) and $R_1$ was 0.0789 (I > 2(I)).

| | |
|---|---|
| Formula | $C_{72}H_{60}ClNdO_{15}P_4S_4$ |
| $D_{calc.}$/ g cm⁻³ | 1.548 |
| $\mu$/mm⁻¹ | 1.080 |
| Formula Weight | 1597.01 |
| Colour | colourless |
| Shape | cut shard |
| Size/mm³ | 0.220×0.140×0.090 |
| $T$/K | 120(2) |
| Crystal System | monoclinic |
| Flack Parameter | 0.029(6) |
| Hooft Parameter | 0.064(7) |
| Space Group | $C2$ |
| $a$/Å | 20.0936(7) |
| $b$/Å | 17.3394(7) |
| $c$/Å | 19.6719(7) |
| $\alpha$/° | 90 |
| $\beta$/° | 90.081(3) |
| $\gamma$/° | 90 |
| V/Å³ | 6853.9(4) |
| Z | 4 |
| Z′ | 1 |
| Wavelength/Å | 0.71073 |
| Radiation type | MoK$_\alpha$ |
| $\Theta_{min}$/° | 3.104 |
| $\Theta_{max}$/° | 27.481 |
| Measured Refl. | 35506 |
| Independent Refl. | 15571 |
| Reflections with I > 2(I) | 12518 |
| $R_{int}$ | 0.0770 |
| Parameters | 877 |
| Restraints | 781 |
| Largest Peak | 5.060 |
| Deepest Hole | -2.450 |
| GooF | 1.084 |
| $wR_2$ (all data) | 0.2016 |
| $wR_2$ | 0.1904 |
| $R_1$ (all data) | 0.1011 |
| $R_1$ | 0.0789 |

## Structure Quality Indicators

**Reflections:**

| d min (Mo) | I/σ | Rint | complete |
|---|---|---|---|
| 0.77 | 9.2 | 7.70% | 100% |

**Refinement:**

| Shift | Max Peak | Min Peak | GooF | Flack |
|---|---|---|---|---|
| 0.000 | 5.1 | -2.5 | 1.084 | .029(6) |

A colourless cut shard-shaped crystal with dimensions 0.220×0.140×0.090 mm$^3$ was mounted on a MITIGEN holder in perfluoroether oil on a Bruker-Nonius FR591 diffractometer equipped with a rotating anode and graphite monochromator and a Bruker-Nonius 95mm CCD camera on κ-goniostat. The crystal was kept at a steady $T$ = 120(2) K during data collection.

Data were measured using MoK$_\alpha$ radiation. The maximum resolution that was achieved was $\Theta$ = 27.481° (0.77 Å).

The diffraction pattern was indexed and the unit cell was refined on 11302 reflections, 90% of the observed reflections.

Data reduction, scaling and absorption corrections were performed using DENZO (Otwinowski, 1997). The final completeness is 99.80 % out to 27.481° in $\Theta$.

An empirical absorption correction was performed using SADABS (Sheldrick, 2003). The absorption coefficient $\mu$ of this material is 1.080 mm$^{-1}$ at this wavelength ($\lambda$ = 0.711Å) and the minimum and maximum transmissions are 0.688 and 1.000.

The structure was solved and the space group $C2$ (# 5) determined by the **ShelXT** (Sheldrick, 2015) structure solution program using Intrinsic Phasing and refined by Least Squares using version 2014/7 of **ShelXL** (Sheldrick, 2015). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. Some restraints were applied.

There is a 2 half molecules in the asymmetric unit, which is represented by the reported sum formula. In other words: Z is 4 and Z' is 1.

The Flack parameter was refined to 0.029(6). Determination of absolute structure using Bayesian statistics on Bijvoet differences using the Olex2 results in 0.064(7). Note: The Flack parameter is used to determine chirality of the crystal studied, the value should be near 0, a value of 1 means that the stereochemistry is wrong and the model should be inverted. A value of 0.5 means that the crystal consists of a racemic mixture of the two enantiomers.

## Reflection Statistics

| | | | |
|---|---|---|---|
| Total reflections (after filtering) | 35506 | Unique reflections | 15571 |
| Completeness | 0.992 | Mean I/$\sigma$ | 8.61 |
| $hkl_{max}$ collected | (26, 22, 25) | $hkl_{min}$ collected | (-26, -22, -25) |
| $hkl_{max}$ used | (26, 22, 25) | $hkl_{min}$ used | (-26, -22, 0) |
| Lim $d_{max}$ collected | 7.0 | Lim $d_{min}$ collected | 0.77 |
| $d_{max}$ used | 6.56 | $d_{min}$ used | 0.77 |
| Friedel pairs | 11196 | Friedel pairs merged | 0 |
| Inconsistent equivalents | 54 | $R_{int}$ | 0.077 |
| $R_{sigma}$ | 0.1085 | Intensity transformed | 0 |
| Omitted reflections | 0 | Omitted by user (OMIT hkl) | 0 |
| Multiplicity | (17172, 6567, 1397, 277, 2) | Maximum multiplicity | 8 |
| Removed systematic absences | 0 | Filtered off (Shel/OMIT) | 109 |

**Table 1**: Bond Lengths in Å.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| Nd1 | O1[1] | 2.379(9) | C17 | C16 | 1.38(2) |
| Nd1 | O1 | 2.379(9) | C2 | C1 | 1.382(19) |
| Nd1 | O3 | 2.535(13) | C34 | C35 | 1.39(2) |
| Nd1 | O4 | 2.413(9) | C26 | C25 | 1.434(19) |
| Nd1 | O4[1] | 2.413(9) | C26 | C27 | 1.40(2) |
| Nd1 | O2 | 2.308(9) | C30 | C25 | 1.37(2) |
| Nd1 | O2[1] | 2.308(9) | C30 | C29 | 1.404(19) |
| P1 | O1 | 1.498(9) | C10 | C11 | 1.37(2) |
| P1 | C7 | 1.801(14) | C11 | C12 | 1.38(2) |
| P1 | C13 | 1.820(13) | C15 | C16 | 1.40(2) |
| P1 | C1 | 1.800(14) | C5 | C4 | 1.40(2) |
| S2 | S2[1] | 2.008(8) | C27 | C28 | 1.36(2) |
| S2 | S1 | 2.123(5) | C28 | C29 | 1.40(2) |
| P2 | C19 | 1.801(14) | Nd2 | O9 | 2.557(14) |
| P2 | O2 | 1.521(9) | Nd2 | O7[2] | 2.366(9) |
| P2 | C31 | 1.787(14) | Nd2 | O7 | 2.365(9) |
| P2 | C25 | 1.791(14) | Nd2 | O8[2] | 2.339(8) |
| S1 | O4 | 1.479(10) | Nd2 | O8 | 2.339(8) |
| S1 | O5 | 1.414(10) | Nd2 | O10[2] | 2.448(10) |
| S1 | O6 | 1.415(12) | Nd2 | O10 | 2.448(10) |
| C19 | C24 | 1.392(19) | S3 | S3[2] | 2.016(9) |
| C19 | C20 | 1.399(19) | S3 | S4 | 2.117(5) |
| C14 | C13 | 1.387(18) | P4 | C67 | 1.801(14) |
| C14 | C15 | 1.396(19) | P4 | O8 | 1.512(9) |
| C32 | C33 | 1.394(17) | P4 | C55 | 1.799(14) |
| C32 | C31 | 1.393(18) | P4 | C61 | 1.804(14) |
| C33 | C34 | 1.38(2) | P3 | O7 | 1.514(9) |
| C7 | C12 | 1.400(19) | P3 | C43 | 1.788(14) |
| C7 | C8 | 1.38(2) | P3 | C49 | 1.802(14) |
| C9 | C10 | 1.40(2) | P3 | C37 | 1.786(14) |
| C9 | C8 | 1.39(2) | S4 | O12 | 1.422(11) |
| C3 | C2 | 1.41(2) | S4 | O10 | 1.475(11) |
| C3 | C4 | 1.37(2) | S4 | O11 | 1.450(12) |
| C24 | C23 | 1.39(2) | C50 | C49 | 1.385(19) |
| C22 | C21 | 1.38(2) | C50 | C51 | 1.398(18) |
| C22 | C23 | 1.38(2) | C43 | C48 | 1.411(18) |
| C21 | C20 | 1.40(2) | C43 | C44 | 1.395(18) |
| C6 | C1 | 1.41(2) | C63 | C62 | 1.385(19) |
| C6 | C5 | 1.39(2) | C63 | C64 | 1.38(2) |
| C13 | C18 | 1.387(18) | C67 | C72 | 1.430(19) |
| C36 | C31 | 1.419(18) | C67 | C68 | 1.34(2) |
| C36 | C35 | 1.36(2) | C38 | C37 | 1.40(2) |
| C17 | C18 | 1.38(2) | C38 | C39 | 1.40(2) |

| Atom | Atom | Length/Å |
|------|------|----------|
| C62 | C61 | 1.375(18) |
| C55 | C60 | 1.380(19) |
| C55 | C56 | 1.411(18) |
| C66 | C61 | 1.401(18) |
| C66 | C65 | 1.391(19) |
| C54 | C49 | 1.39(2) |
| C54 | C53 | 1.40(2) |
| C60 | C59 | 1.388(19) |
| C42 | C41 | 1.39(2) |
| C42 | C37 | 1.41(2) |
| C71 | C72 | 1.39(2) |
| C71 | C70 | 1.33(2) |
| C56 | C57 | 1.36(2) |
| C51 | C52 | 1.36(2) |
| C47 | C48 | 1.39(2) |
| C47 | C46 | 1.39(2) |
| C46 | C45 | 1.39(2) |
| C41 | C40 | 1.40(2) |

| Atom | Atom | Length/Å |
|------|------|----------|
| C70 | C69 | 1.37(3) |
| C44 | C45 | 1.39(2) |
| C52 | C53 | 1.41(2) |
| C40 | C39 | 1.36(2) |
| C57 | C58 | 1.38(2) |
| C58 | C59 | 1.40(2) |
| C64 | C65 | 1.38(2) |
| C68 | C69 | 1.39(2) |
| Cl1 | O14 | 1.411(15) |
| Cl1 | O14[1] | 1.411(15) |
| Cl1 | O13[1] | 1.407(18) |
| Cl1 | O13 | 1.407(18) |
| Cl2 | O16[2] | 1.457(16) |
| Cl2 | O16 | 1.457(16) |
| Cl2 | O15[2] | 1.392(17) |
| Cl2 | O15 | 1.392(17) |

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[1]-x,+y,1-z; [2]1-x,+y,-z

**Table 2**: Bond Angles in °.

| Atom | Atom | Atom | Angle/° |
|------|------|------|---------|
| O1[1] | Nd1 | O1 | 153.8(4) |
| O1[1] | Nd1 | O3 | 76.9(2) |
| O1 | Nd1 | O3 | 76.9(2) |
| O1[1] | Nd1 | O4 | 127.0(3) |
| O1 | Nd1 | O4[1] | 127.0(3) |
| O1 | Nd1 | O4 | 76.1(3) |
| O1[1] | Nd1 | O4[1] | 76.1(3) |
| O4 | Nd1 | O3 | 143.0(2) |
| O4[1] | Nd1 | O3 | 143.0(2) |
| O4 | Nd1 | O4[1] | 74.1(5) |
| O2[1] | Nd1 | O1[1] | 83.4(3) |
| O2 | Nd1 | O1 | 83.4(3) |
| O2 | Nd1 | O1[1] | 90.7(3) |
| O2[1] | Nd1 | O1 | 90.7(3) |
| O2[1] | Nd1 | O3 | 77.0(2) |
| O2 | Nd1 | O3 | 77.0(2) |
| O2 | Nd1 | O4 | 124.1(3) |
| O2[1] | Nd1 | O4[1] | 124.1(3) |
| O2[1] | Nd1 | O4 | 78.4(3) |
| O2 | Nd1 | O4[1] | 78.4(3) |
| O2[1] | Nd1 | O2 | 154.0(4) |
| O1 | P1 | C7 | 114.5(6) |
| O1 | P1 | C13 | 108.7(6) |
| O1 | P1 | C1 | 110.5(6) |
| C7 | P1 | C13 | 108.7(6) |
| C1 | P1 | C7 | 105.5(6) |
| C1 | P1 | C13 | 108.8(6) |
| S2[1] | S2 | S1 | 104.2(2) |
| O2 | P2 | C19 | 110.0(6) |
| O2 | P2 | C31 | 112.8(6) |
| O2 | P2 | C25 | 110.2(6) |
| C31 | P2 | C19 | 106.5(6) |
| C31 | P2 | C25 | 109.6(6) |
| C25 | P2 | C19 | 107.5(6) |
| O4 | S1 | S2 | 103.9(4) |
| O5 | S1 | S2 | 101.5(5) |
| O5 | S1 | O4 | 112.5(7) |
| O5 | S1 | O6 | 117.0(8) |
| O6 | S1 | S2 | 109.3(5) |

| Atom | Atom | Atom | Angle/° |
|------|------|------|---------|
| O6 | S1 | O4 | 111.3(7) |
| P1 | O1 | Nd1 | 171.2(6) |
| S1 | O4 | Nd1 | 137.3(6) |
| C24 | C19 | P2 | 118.0(10) |
| C24 | C19 | C20 | 120.0(13) |
| C20 | C19 | P2 | 122.0(11) |
| C13 | C14 | C15 | 118.8(13) |
| C31 | C32 | C33 | 121.3(13) |
| C34 | C33 | C32 | 118.6(14) |
| C12 | C7 | P1 | 121.3(11) |
| C8 | C7 | P1 | 119.1(10) |
| C8 | C7 | C12 | 119.6(13) |
| C8 | C9 | C10 | 119.9(14) |
| C4 | C3 | C2 | 120.4(15) |
| P2 | O2 | Nd1 | 172.6(6) |
| C23 | C24 | C19 | 119.2(14) |
| C23 | C22 | C21 | 121.3(15) |
| C22 | C21 | C20 | 118.5(14) |
| C5 | C6 | C1 | 120.3(14) |
| C14 | C13 | P1 | 117.2(10) |
| C14 | C13 | C18 | 121.3(12) |
| C18 | C13 | P1 | 121.5(10) |
| C35 | C36 | C31 | 120.3(13) |
| C18 | C17 | C16 | 119.4(14) |
| C17 | C18 | C13 | 119.9(13) |
| C1 | C2 | C3 | 119.5(15) |
| C6 | C1 | P1 | 121.2(10) |
| C2 | C1 | P1 | 119.0(11) |
| C2 | C1 | C6 | 119.8(13) |
| C33 | C34 | C35 | 121.2(15) |
| C32 | C31 | P2 | 122.3(10) |
| C32 | C31 | C36 | 118.3(13) |
| C36 | C31 | P2 | 119.3(10) |
| C27 | C26 | C25 | 118.1(14) |
| C25 | C30 | C29 | 120.4(14) |
| C11 | C10 | C9 | 119.0(14) |
| C10 | C11 | C12 | 121.8(15) |
| C14 | C15 | C16 | 119.6(13) |
| C6 | C5 | C4 | 119.4(16) |

| Atom | Atom | Atom | Angle/° |
|---|---|---|---|
| C11 | C12 | C7 | 119.1(14) |
| C17 | C16 | C15 | 120.9(14) |
| C26 | C25 | P2 | 117.3(11) |
| C30 | C25 | P2 | 123.0(11) |
| C30 | C25 | C26 | 119.7(13) |
| C28 | C27 | C26 | 121.9(14) |
| C27 | C28 | C29 | 119.9(13) |
| C22 | C23 | C24 | 120.6(15) |
| C36 | C35 | C34 | 120.2(13) |
| C28 | C29 | C30 | 119.8(14) |
| C19 | C20 | C21 | 120.3(14) |
| C7 | C8 | C9 | 120.6(13) |
| O7 | Nd2 | O9 | 74.2(2) |
| O7[2] | Nd2 | O9 | 74.2(2) |
| O7 | Nd2 | O7[2] | 148.4(4) |
| O7[2] | Nd2 | O10[2] | 77.5(3) |
| O7 | Nd2 | O10[2] | 130.1(3) |
| O7[2] | Nd2 | O10 | 130.1(3) |
| O7 | Nd2 | O10 | 77.5(3) |
| O8[2] | Nd2 | O9 | 75.5(2) |
| O8 | Nd2 | O9 | 75.5(2) |
| O8[2] | Nd2 | O7[2] | 85.8(3) |
| O8[2] | Nd2 | O7 | 86.3(3) |
| O8 | Nd2 | O7 | 85.8(3) |
| O8 | Nd2 | O7[2] | 86.3(3) |
| O8 | Nd2 | O8[2] | 151.0(5) |
| O8 | Nd2 | O10 | 77.2(3) |
| O8 | Nd2 | O10[2] | 128.0(4) |
| O8[2] | Nd2 | O10[2] | 77.2(3) |
| O8[2] | Nd2 | O10 | 128.0(4) |
| O10[2] | Nd2 | O9 | 141.6(2) |
| O10 | Nd2 | O9 | 141.6(2) |
| O10 | Nd2 | O10[2] | 76.7(5) |
| S3[2] | S3 | S4 | 104.4(3) |
| C67 | P4 | C61 | 108.4(6) |
| O8 | P4 | C67 | 110.3(6) |
| O8 | P4 | C55 | 111.5(6) |
| O8 | P4 | C61 | 110.6(6) |
| C55 | P4 | C67 | 106.9(6) |
| C55 | P4 | C61 | 109.0(6) |
| O7 | P3 | C43 | 110.4(6) |
| O7 | P3 | C49 | 110.7(6) |
| O7 | P3 | C37 | 113.6(6) |
| C43 | P3 | C49 | 109.2(6) |
| C37 | P3 | C43 | 108.7(7) |
| C37 | P3 | C49 | 104.1(6) |
| O12 | S4 | S3 | 100.9(4) |
| O12 | S4 | O10 | 112.2(6) |
| O12 | S4 | O11 | 115.9(7) |
| O10 | S4 | S3 | 104.1(5) |
| O11 | S4 | S3 | 108.9(6) |
| O11 | S4 | O10 | 113.2(8) |
| P3 | O7 | Nd2 | 166.0(6) |
| C49 | C50 | C51 | 120.7(14) |
| C48 | C43 | P3 | 118.3(10) |
| C44 | C43 | P3 | 122.0(11) |
| C44 | C43 | C48 | 119.7(13) |
| C64 | C63 | C62 | 120.7(13) |
| C72 | C67 | P4 | 122.0(11) |
| C68 | C67 | P4 | 119.0(11) |
| C68 | C67 | C72 | 118.5(13) |
| P4 | O8 | Nd2 | 164.9(6) |
| C39 | C38 | C37 | 119.0(16) |
| C61 | C62 | C63 | 120.3(14) |
| C60 | C55 | P4 | 122.7(11) |
| C60 | C55 | C56 | 118.2(13) |
| C56 | C55 | P4 | 118.9(10) |
| C65 | C66 | C61 | 119.6(13) |
| S4 | O10 | Nd2 | 133.0(7) |
| C49 | C54 | C53 | 120.5(13) |
| C55 | C60 | C59 | 121.6(14) |
| C41 | C42 | C37 | 120.0(14) |
| C50 | C49 | P3 | 119.9(11) |
| C50 | C49 | C54 | 119.1(13) |
| C54 | C49 | P3 | 120.9(10) |
| C70 | C71 | C72 | 119.5(15) |
| C57 | C56 | C55 | 120.5(13) |
| C52 | C51 | C50 | 120.3(13) |
| C48 | C47 | C46 | 120.0(15) |
| C47 | C48 | C43 | 119.6(14) |
| C47 | C46 | C45 | 121.0(16) |
| C42 | C41 | C40 | 119.1(16) |
| C62 | C61 | P4 | 118.8(11) |
| C62 | C61 | C66 | 119.6(13) |
| C66 | C61 | P4 | 121.5(10) |
| C71 | C72 | C67 | 119.5(15) |
| C71 | C70 | C69 | 122.4(16) |
| C45 | C44 | C43 | 120.6(14) |
| C38 | C37 | P3 | 123.1(12) |
| C38 | C37 | C42 | 119.8(14) |
| C42 | C37 | P3 | 117.1(11) |
| C51 | C52 | C53 | 120.2(13) |
| C39 | C40 | C41 | 121.5(15) |
| C56 | C57 | C58 | 120.9(15) |
| C54 | C53 | C52 | 119.1(14) |
| C57 | C58 | C59 | 120.0(15) |
| C65 | C64 | C63 | 119.3(13) |
| C40 | C39 | C38 | 120.6(15) |
| C67 | C68 | C69 | 121.5(16) |
| C60 | C59 | C58 | 118.8(15) |
| C46 | C45 | C44 | 119.0(15) |
| O14[1] | Cl1 | O14 | 109.1(14) |
| O13 | Cl1 | O14 | 111.7(12) |
| O13[1] | Cl1 | O14 | 107.3(12) |
| O13[1] | Cl1 | O14[1] | 111.7(12) |
| O13 | Cl1 | O14[1] | 107.3(12) |
| O13 | Cl1 | O13[1] | 110(2) |
| O16 | Cl2 | O16[2] | 105.6(13) |
| O15 | Cl2 | O16 | 108.1(10) |
| O15[2] | Cl2 | O16 | 110.2(12) |
| O15[2] | Cl2 | O16[2] | 108.1(10) |
| O15 | Cl2 | O16[2] | 110.2(12) |
| O15 | Cl2 | O15[2] | 114.2(18) |
| C3 | C4 | C5 | 120.5(14) |
| C64 | C65 | C66 | 120.5(14) |
| C70 | C69 | C68 | 118.4(18) |

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[1]-x,+y,1-z; [2]1-x,+y,-z

# Crystal Data and Experimental [Er(Ph$_3$PO)$_2$(H$_2$O)$_5$]·5(Ph$_3$PO)·3[ClO$_4$]
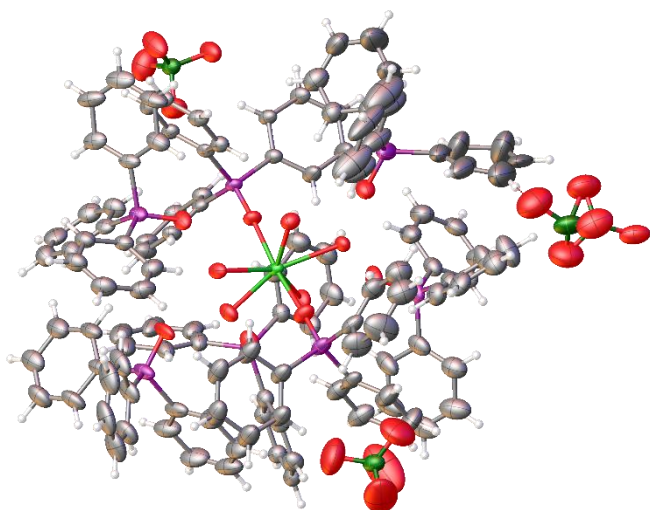


**Figure 1:** Thermal ellipsoids drawn at the 50% probability level.

**Experimental.** A suitable colourless block-shaped crystal (0.120×0.080×0.040 mm$^3$) was selected and mounted on a suitable support on the Daresbury SRS station 9.8 diffractometer. The crystal was kept at a steady $T$ = 120(2) K during data collection. The structure was solved with the **ShelXT** (Sheldrick, 2015) structure solution program using the Intrinsic Phasing solution method and by using **Olex2** (Dolomanov et al., 2009) as the graphical interface. The model was refined with version 2014/7 of **ShelXL** (Sheldrick, 2015) using Least Squares minimisation.

**Crystal Data.** C$_{126}$H$_{105}$Cl$_{2.5}$ErO$_{22}$P$_7$, $M_r$ = 2443.77, orthorhombic, *Pbcn* (No. 60), a = 43.152(15) Å, b = 23.773(8) Å, c = 23.799(8) Å, $\alpha$ = $\beta$ = $\gamma$ = 90°, $V$ = 24414(14) Å$^3$, $T$ = 120(2) K, $Z$ = 8, $Z'$ = 1, $\mu$ = 0.844 mm$^{-1}$, 174628 reflections measured, 21554 unique ($R_{int}$ = 0.0711) which were used in all calculations. The final $wR_2$ was 0.1731 (all data) and $R_1$ was 0.0781 (I > 2(I)).

| | |
|---|---|
| Formula | C$_{126}$H$_{105}$Cl$_{2.5}$ErO$_{22}$P$_7$ |
| $D_{calc.}$/ g cm$^{-3}$ | 1.330 |
| $\mu$/mm$^{-1}$ | 0.844 |
| Formula Weight | 2443.77 |
| Colour | colourless |
| Shape | block |
| Size/mm$^3$ | 0.120×0.080×0.040 |
| $T$/K | 120(2) |
| Crystal System | orthorhombic |
| Space Group | *Pbcn* |
| a/Å | 43.152(15) |
| b/Å | 23.773(8) |
| c/Å | 23.799(8) |
| $\alpha$/° | 90 |
| $\beta$/° | 90 |
| $\gamma$/° | 90 |
| V/Å$^3$ | 24414(14) |
| Z | 8 |
| Z' | 1 |
| Wavelength/Å | 0.6911 |
| Radiation type | ? |
| $\Theta_{min}$/° | 2.181 |
| $\Theta_{max}$/° | 24.291 |
| Measured Refl. | 174628 |
| Independent Refl. | 21554 |
| Reflections with I > 2(I) | 18416 |
| $R_{int}$ | 0.0711 |
| Parameters | 1447 |
| Restraints | 1273 |
| Largest Peak | 1.460 |
| Deepest Hole | -2.420 |
| GooF | 1.200 |
| $wR_2$ (all data) | 0.1731 |
| $wR_2$ | 0.1675 |
| $R_1$ (all data) | 0.0894 |
| $R_1$ | 0.0781 |

## Structure Quality Indicators

**Reflections:** | d min (0.6911) **0.84** | I/σ **25.9** | Rint **7.11%** | complete **100%**

**Refinement:** | Shift **0.003** | Max Peak **1.5** | Min Peak **-2.4** | GooF **1.200**

A colourless block-shaped crystal with dimensions 0.120×0.080×0.040 mm³ was mounted on a suitable support. Data were collected using the Daresbury SRS station 9.8 diffractometer, equipped with a Si(111) monochromator and Bruker SMART APEX2 CCD detector (Bruker, 2004), and operating at $T$ = 120(2) K.

Data were measured using synchrotron radiation at a wavelength of 0.6911 Å. The maximum resolution that was achieved was $\Theta$ = 24.291° (0.84 Å).

The diffraction pattern was indexed using SAINT (Bruker, 2004) and the unit cell was refined on 977 reflections, 5% of the observed reflections.

Data reduction, scaling and absorption corrections were performed using Bruker SAINT. The final completeness is 99.80 % out to 24.291° in $\Theta$. An empirical absorption correction was performed using SADABS (Bruker, 2004). The absorption coefficient $\mu$ of this material is 0.844 mm$^{-1}$ at this wavelength ($\lambda$ = 0.6911 Å) and the minimum and maximum transmissions are 1.000 and 0.860.

The structure was solved and the space group *Pbcn* (# 60) determined by the **ShelXT** (Sheldrick, 2015) structure solution program using Intrinsic Phasing and refined by Least Squares using version 2014/7 of **ShelXL** (Sheldrick, 2015). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. There are some small cavities available for solvents. No solvents were identified, possibly some water molecules, so the structure was SQUEEZEd.

There is a single molecule in the asymmetric unit, which is represented by the reported sum formula. In other words: Z is 8 and Z' is 1.

## Reflection Statistics

| | | | |
|---|---|---|---|
| Total reflections (after filtering) | 181102 | Unique reflections | 21554 |
| Completeness | 0.999 | Mean I/$\sigma$ | 17.04 |
| hkl$_{max}$ collected | (51, 28, 28) | hkl$_{min}$ collected | (-51, -28, -28) |
| hkl$_{max}$ used | (51, 28, 28) | hkl$_{min}$ used | (0, 0, 0) |
| Lim d$_{max}$ collected | 10.0 | Lim d$_{min}$ collected | 0.83 |
| d$_{max}$ used | 9.16 | d$_{min}$ used | 0.84 |
| Friedel pairs | 71278 | Friedel pairs merged | 1 |
| Inconsistent equivalents | 0 | R$_{int}$ | 0.0711 |
| R$_{sigma}$ | 0.0386 | Intensity transformed | 0 |
| Omitted reflections | 0 | Omitted by user (OMIT hkl) | 0 |
| Multiplicity | (133767, 22292, 917) | Maximum multiplicity | 12 |
| Removed systematic absences | 6474 | Filtered off (Shel/OMIT) | 0 |

**Table 1**: Bond Lengths in Å.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| Er1 | O1 | 2.170(5) | P1 | C1 | 1.784(10) |
| Er1 | O2 | 2.188(5) | P1 | C7 | 1.796(8) |
| Er1 | O8 | 2.344(5) | P1 | C13 | 1.788(8) |
| Er1 | O9 | 2.337(5) | P2 | O2 | 1.502(5) |
| Er1 | O10 | 2.320(5) | P2 | C19 | 1.802(7) |
| Er1 | O11 | 2.312(5) | P2 | C25 | 1.782(8) |
| Er1 | O12 | 2.374(4) | P2 | C31 | 1.798(7) |
| P1 | O1 | 1.511(5) | C1 | C2 | 1.383(13) |

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|------|------|----------|------|------|----------|
| C1 | C6 | 1.398(12) | C43 | C48 | 1.418(11) |
| C2 | C3 | 1.363(14) | C44 | C45 | 1.399(12) |
| C3 | C4 | 1.408(15) | C45 | C46 | 1.401(13) |
| C4 | C5 | 1.390(17) | C46 | C47 | 1.362(13) |
| C5 | C6 | 1.363(16) | C47 | C48 | 1.368(13) |
| C7 | C8 | 1.397(12) | C49 | C50 | 1.402(12) |
| C7 | C12 | 1.376(11) | C49 | C54 | 1.370(12) |
| C8 | C9 | 1.384(12) | C50 | C51 | 1.412(11) |
| C9 | C10 | 1.399(13) | C51 | C52 | 1.352(15) |
| C10 | C11 | 1.372(14) | C52 | C53 | 1.369(15) |
| C11 | C12 | 1.360(12) | C53 | C54 | 1.425(12) |
| C13 | C14 | 1.369(12) | P4 | O4 | 1.498(5) |
| C13 | C18 | 1.393(13) | P4 | C55 | 1.805(9) |
| C14 | C15 | 1.402(14) | P4 | C61 | 1.802(10) |
| C15 | C16 | 1.396(15) | P4 | C67 | 1.816(8) |
| C16 | C17 | 1.365(14) | C55 | C56 | 1.413(13) |
| C17 | C18 | 1.384(12) | C55 | C60 | 1.378(13) |
| C19 | C20 | 1.393(10) | C56 | C57 | 1.393(15) |
| C19 | C24 | 1.398(10) | C57 | C58 | 1.351(17) |
| C20 | C21 | 1.390(10) | C58 | C59 | 1.370(16) |
| C21 | C22 | 1.369(11) | C59 | C60 | 1.404(13) |
| C22 | C23 | 1.392(11) | C61 | C62 | 1.382(11) |
| C23 | C24 | 1.392(10) | C61 | C66 | 1.397(12) |
| C25 | C26 | 1.389(10) | C62 | C63 | 1.383(14) |
| C25 | C30 | 1.386(10) | C63 | C64 | 1.361(14) |
| C26 | C27 | 1.372(11) | C64 | C65 | 1.369(13) |
| C27 | C28 | 1.378(11) | C65 | C66 | 1.383(14) |
| C28 | C29 | 1.385(11) | C67 | C68 | 1.391(14) |
| C29 | C30 | 1.389(11) | C67 | C72 | 1.373(13) |
| C31 | C32 | 1.383(9) | C68 | C69 | 1.406(13) |
| C31 | C36 | 1.384(10) | C69 | C70 | 1.371(15) |
| C32 | C33 | 1.384(10) | C70 | C71 | 1.348(16) |
| C33 | C34 | 1.365(11) | C71 | C72 | 1.410(13) |
| C34 | C35 | 1.364(11) | P5 | O5 | 1.496(5) |
| C35 | C36 | 1.396(11) | P5 | C73 | 1.795(8) |
| Cl1 | O13 | 1.437(6) | P5 | C79 | 1.790(8) |
| Cl1 | O14 | 1.412(7) | P5 | C85 | 1.790(8) |
| Cl1 | O15 | 1.412(7) | C73 | C74 | 1.394(11) |
| Cl1 | O16 | 1.416(8) | C73 | C78 | 1.368(12) |
| Cl2 | O17¹ | 1.368(9) | C74 | C75 | 1.386(13) |
| Cl2 | O17 | 1.369(9) | C75 | C76 | 1.358(16) |
| Cl2 | O18 | 1.329(10) | C76 | C77 | 1.331(16) |
| Cl2 | O18¹ | 1.329(10) | C77 | C78 | 1.407(12) |
| Cl3 | O19 | 1.370(9) | C79 | C80 | 1.389(11) |
| Cl3 | O20 | 1.484(10) | C79 | C84 | 1.384(10) |
| Cl3 | O21 | 1.467(11) | C80 | C81 | 1.384(12) |
| Cl3 | O22 | 1.381(15) | C81 | C82 | 1.385(11) |
| Cl3A | O19 | 1.573(12) | C82 | C83 | 1.383(11) |
| Cl3A | O20 | 1.417(12) | C83 | C84 | 1.402(11) |
| Cl3A | O21 | 1.233(12) | C85 | C86 | 1.381(11) |
| Cl3A | O22A | 1.409(17) | C85 | C90 | 1.366(11) |
| P3 | O3 | 1.500(5) | C86 | C87 | 1.390(12) |
| P3 | C37 | 1.796(8) | C87 | C88 | 1.374(13) |
| P3 | C43 | 1.783(8) | C88 | C89 | 1.367(13) |
| P3 | C49 | 1.807(7) | C89 | C90 | 1.405(12) |
| C37 | C38 | 1.379(11) | P6 | O6 | 1.508(6) |
| C37 | C42 | 1.405(11) | P6 | C91 | 1.778(9) |
| C38 | C39 | 1.394(12) | P6 | C97 | 1.798(9) |
| C39 | C40 | 1.391(13) | P6 | C103 | 1.778(9) |
| C40 | C41 | 1.354(13) | C91 | C92 | 1.393(13) |
| C41 | C42 | 1.382(11) | C91 | C96 | 1.397(11) |
| C43 | C44 | 1.370(11) | C92 | C93 | 1.377(13) |

| Atom | Atom | Length/Å |
|------|------|----------|
| C93 | C94 | 1.373(13) |
| C94 | C95 | 1.378(14) |
| C95 | C96 | 1.396(12) |
| C97 | C98 | 1.396(13) |
| C97 | C102 | 1.408(14) |
| C98 | C99 | 1.399(14) |
| C99 | C100 | 1.370(17) |
| C100 | C101 | 1.369(16) |
| C101 | C102 | 1.398(13) |
| C103 | C104 | 1.390(12) |
| C103 | C108 | 1.385(12) |
| C104 | C105 | 1.378(14) |
| C105 | C106 | 1.378(14) |
| C106 | C107 | 1.353(14) |
| C107 | C108 | 1.420(13) |
| P7 | O7 | 1.495(6) |
| P7 | C109 | 1.782(10) |
| P7 | C115 | 1.766(12) |
| P7 | C121 | 1.803(13) |
| C109 | C110 | 1.359(13) |

| Atom | Atom | Length/Å |
|------|------|----------|
| C109 | C114 | 1.397(15) |
| C110 | C111 | 1.392(13) |
| C111 | C112 | 1.358(15) |
| C112 | C113 | 1.372(19) |
| C113 | C114 | 1.398(19) |
| C115 | C116 | 1.41(2) |
| C115 | C120 | 1.394(19) |
| C116 | C117 | 1.47(2) |
| C117 | C118 | 1.52(3) |
| C118 | C119 | 1.35(3) |
| C119 | C120 | 1.31(2) |
| C121 | C122 | 1.405(17) |
| C121 | C126 | 1.350(19) |
| C122 | C123 | 1.36(2) |
| C123 | C124 | 1.36(3) |
| C124 | C125 | 1.47(2) |
| C125 | C126 | 1.445(18) |

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[1]1-x,+y,1/2-z

**Table 3**: Bond Angles in °.

| Atom | Atom | Atom | Angle/° |
|------|------|------|---------|
| O1 | Er1 | O2 | 172.5(2) |
| O1 | Er1 | O8 | 87.0(2) |
| O1 | Er1 | O9 | 89.61(19) |
| O1 | Er1 | O10 | 96.3(2) |
| O1 | Er1 | O11 | 92.2(2) |
| O1 | Er1 | O12 | 86.30(19) |
| O2 | Er1 | O8 | 86.08(18) |
| O2 | Er1 | O9 | 91.74(18) |
| O2 | Er1 | O10 | 91.14(19) |
| O2 | Er1 | O11 | 91.53(19) |
| O2 | Er1 | O12 | 88.72(17) |
| O8 | Er1 | O12 | 71.74(17) |
| O9 | Er1 | O8 | 77.07(18) |
| O9 | Er1 | O12 | 148.71(17) |
| O10 | Er1 | O8 | 147.70(18) |
| O10 | Er1 | O9 | 70.84(18) |
| O10 | Er1 | O12 | 140.45(17) |
| O11 | Er1 | O8 | 143.06(18) |
| O11 | Er1 | O9 | 139.86(18) |
| O11 | Er1 | O10 | 69.10(17) |
| O11 | Er1 | O12 | 71.36(17) |
| O1 | P1 | C1 | 111.1(4) |
| O1 | P1 | C7 | 110.1(4) |
| O1 | P1 | C13 | 109.5(3) |
| C1 | P1 | C7 | 108.0(4) |
| C1 | P1 | C13 | 108.3(4) |
| C13 | P1 | C7 | 109.8(4) |
| O2 | P2 | C19 | 110.0(3) |
| O2 | P2 | C25 | 110.7(3) |
| O2 | P2 | C31 | 109.2(3) |
| C25 | P2 | C19 | 108.6(3) |
| C25 | P2 | C31 | 110.6(3) |
| C31 | P2 | C19 | 107.8(3) |
| P1 | O1 | Er1 | 177.0(4) |
| P2 | O2 | Er1 | 176.2(3) |
| C2 | C1 | P1 | 120.1(7) |

| Atom | Atom | Atom | Angle/° |
|------|------|------|---------|
| C2 | C1 | C6 | 120.4(10) |
| C6 | C1 | P1 | 119.4(8) |
| C3 | C2 | C1 | 121.0(9) |
| C2 | C3 | C4 | 118.8(11) |
| C5 | C4 | C3 | 119.8(12) |
| C6 | C5 | C4 | 121.0(12) |
| C5 | C6 | C1 | 118.9(11) |
| C8 | C7 | P1 | 121.9(6) |
| C12 | C7 | P1 | 118.5(7) |
| C12 | C7 | C8 | 119.5(8) |
| C9 | C8 | C7 | 119.7(8) |
| C8 | C9 | C10 | 119.0(9) |
| C11 | C10 | C9 | 120.8(9) |
| C12 | C11 | C10 | 119.5(9) |
| C11 | C12 | C7 | 121.4(9) |
| C14 | C13 | P1 | 122.4(8) |
| C14 | C13 | C18 | 120.0(8) |
| C18 | C13 | P1 | 117.5(6) |
| C13 | C14 | C15 | 118.9(10) |
| C16 | C15 | C14 | 120.6(10) |
| C17 | C16 | C15 | 119.8(9) |
| C16 | C17 | C18 | 119.7(10) |
| C17 | C18 | C13 | 120.9(9) |
| C20 | C19 | P2 | 117.8(5) |
| C20 | C19 | C24 | 121.0(6) |
| C24 | C19 | P2 | 121.2(5) |
| C21 | C20 | C19 | 118.6(7) |
| C22 | C21 | C20 | 121.2(8) |
| C21 | C22 | C23 | 120.1(7) |
| C24 | C23 | C22 | 120.2(7) |
| C23 | C24 | C19 | 118.8(7) |
| C26 | C25 | P2 | 117.5(5) |
| C30 | C25 | P2 | 123.1(6) |
| C30 | C25 | C26 | 119.4(7) |
| C27 | C26 | C25 | 120.4(7) |
| C26 | C27 | C28 | 120.8(8) |

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|------|------|------|---------|------|------|------|---------|
| C27 | C28 | C29 | 119.1(8) | C51 | C52 | C53 | 122.4(9) |
| C28 | C29 | C30 | 120.7(8) | C52 | C53 | C54 | 118.2(10) |
| C25 | C30 | C29 | 119.6(7) | C49 | C54 | C53 | 119.9(10) |
| C32 | C31 | P2 | 121.9(5) | O4 | P4 | C55 | 111.8(4) |
| C32 | C31 | C36 | 120.6(7) | O4 | P4 | C61 | 110.6(4) |
| C36 | C31 | P2 | 117.4(5) | O4 | P4 | C67 | 112.7(3) |
| C31 | C32 | C33 | 119.3(7) | C55 | P4 | C67 | 106.1(4) |
| C34 | C33 | C32 | 120.2(7) | C61 | P4 | C55 | 108.0(4) |
| C35 | C34 | C33 | 120.9(8) | C61 | P4 | C67 | 107.4(4) |
| C34 | C35 | C36 | 120.1(8) | C56 | C55 | P4 | 117.0(8) |
| C31 | C36 | C35 | 118.9(7) | C60 | C55 | P4 | 122.5(7) |
| O14 | Cl1 | O13 | 111.0(4) | C60 | C55 | C56 | 120.5(9) |
| O14 | Cl1 | O15 | 110.7(5) | C57 | C56 | C55 | 117.7(11) |
| O14 | Cl1 | O16 | 110.1(5) | C58 | C57 | C56 | 120.8(12) |
| O15 | Cl1 | O13 | 108.9(4) | C57 | C58 | C59 | 122.5(11) |
| O15 | Cl1 | O16 | 104.8(5) | C58 | C59 | C60 | 118.1(12) |
| O16 | Cl1 | O13 | 111.2(5) | C55 | C60 | C59 | 120.3(10) |
| O17[1] | Cl2 | O17 | 115.5(10) | C62 | C61 | P4 | 121.5(8) |
| O18[1] | Cl2 | O17 | 105.5(7) | C62 | C61 | C66 | 119.7(10) |
| O18 | Cl2 | O17 | 109.0(8) | C66 | C61 | P4 | 118.8(6) |
| O18 | Cl2 | O17[1] | 105.5(7) | C61 | C62 | C63 | 119.8(9) |
| O18[1] | Cl2 | O17[1] | 109.0(8) | C64 | C63 | C62 | 120.1(9) |
| O18 | Cl2 | O18[1] | 112.7(16) | C63 | C64 | C65 | 121.1(11) |
| O19 | Cl3 | O20 | 108.2(7) | C64 | C65 | C66 | 119.9(10) |
| O19 | Cl3 | O21 | 107.6(7) | C65 | C66 | C61 | 119.5(8) |
| O19 | Cl3 | O22 | 112.8(8) | C68 | C67 | P4 | 115.8(7) |
| O21 | Cl3 | O20 | 105.3(8) | C72 | C67 | P4 | 122.7(8) |
| O22 | Cl3 | O20 | 110.8(7) | C72 | C67 | C68 | 121.5(9) |
| O22 | Cl3 | O21 | 111.8(7) | C67 | C68 | C69 | 118.3(10) |
| O20 | Cl3A | O19 | 101.2(9) | C70 | C69 | C68 | 119.7(12) |
| O21 | Cl3A | O19 | 108.8(9) | C71 | C70 | C69 | 121.5(10) |
| O21 | Cl3A | O20 | 124.5(10) | C70 | C71 | C72 | 120.3(11) |
| O21 | Cl3A | O22A | 121.8(16) | C67 | C72 | C71 | 118.5(11) |
| O22A | Cl3A | O19 | 89.8(13) | O5 | P5 | C73 | 111.8(4) |
| O22A | Cl3A | O20 | 103.5(14) | O5 | P5 | C79 | 110.4(3) |
| O3 | P3 | C37 | 110.3(4) | O5 | P5 | C85 | 111.4(3) |
| O3 | P3 | C43 | 113.7(3) | C79 | P5 | C73 | 107.8(4) |
| O3 | P3 | C49 | 109.4(3) | C79 | P5 | C85 | 109.0(4) |
| C37 | P3 | C49 | 107.3(3) | C85 | P5 | C73 | 106.4(4) |
| C43 | P3 | C37 | 109.5(4) | C74 | C73 | P5 | 119.6(7) |
| C43 | P3 | C49 | 106.4(4) | C78 | C73 | P5 | 122.0(7) |
| C38 | C37 | P3 | 119.0(6) | C78 | C73 | C74 | 118.4(8) |
| C38 | C37 | C42 | 119.8(8) | C75 | C74 | C73 | 120.4(10) |
| C42 | C37 | P3 | 121.3(6) | C76 | C75 | C74 | 120.5(11) |
| C37 | C38 | C39 | 120.4(8) | C77 | C76 | C75 | 119.5(11) |
| C40 | C39 | C38 | 119.3(9) | C76 | C77 | C78 | 122.0(12) |
| C41 | C40 | C39 | 120.0(9) | C73 | C78 | C77 | 119.2(10) |
| C40 | C41 | C42 | 121.9(9) | C80 | C79 | P5 | 118.7(6) |
| C41 | C42 | C37 | 118.6(8) | C84 | C79 | P5 | 122.1(6) |
| C44 | C43 | P3 | 125.2(6) | C84 | C79 | C80 | 119.2(7) |
| C44 | C43 | C48 | 118.5(8) | C81 | C80 | C79 | 120.8(8) |
| C48 | C43 | P3 | 116.2(6) | C80 | C81 | C82 | 119.7(8) |
| C43 | C44 | C45 | 120.7(8) | C83 | C82 | C81 | 120.4(8) |
| C44 | C45 | C46 | 119.2(9) | C82 | C83 | C84 | 119.5(8) |
| C47 | C46 | C45 | 120.7(9) | C79 | C84 | C83 | 120.4(7) |
| C46 | C47 | C48 | 120.0(9) | C86 | C85 | P5 | 123.8(6) |
| C47 | C48 | C43 | 121.1(8) | C90 | C85 | P5 | 117.1(6) |
| C50 | C49 | P3 | 121.2(6) | C90 | C85 | C86 | 119.1(8) |
| C54 | C49 | P3 | 117.7(7) | C85 | C86 | C87 | 118.7(9) |
| C54 | C49 | C50 | 121.1(8) | C88 | C87 | C86 | 121.8(8) |
| C49 | C50 | C51 | 117.8(9) | C89 | C88 | C87 | 120.0(9) |
| C52 | C51 | C50 | 120.6(10) | C88 | C89 | C90 | 118.0(9) |

| Atom | Atom | Atom | Angle/° |
|------|------|------|---------|
| C85 | C90 | C89 | 122.4(8) |
| O6 | P6 | C91 | 109.7(4) |
| O6 | P6 | C97 | 113.0(4) |
| O6 | P6 | C103 | 109.2(4) |
| C91 | P6 | C97 | 106.0(4) |
| C91 | P6 | C103 | 111.1(4) |
| C103 | P6 | C97 | 107.9(5) |
| C92 | C91 | P6 | 120.0(6) |
| C92 | C91 | C96 | 117.6(8) |
| C96 | C91 | P6 | 122.4(7) |
| C93 | C92 | C91 | 121.9(9) |
| C94 | C93 | C92 | 120.0(10) |
| C93 | C94 | C95 | 119.7(9) |
| C94 | C95 | C96 | 120.6(9) |
| C95 | C96 | C91 | 120.2(9) |
| C98 | C97 | P6 | 118.6(8) |
| C98 | C97 | C102 | 121.0(9) |
| C102 | C97 | P6 | 120.3(7) |
| C97 | C98 | C99 | 118.3(12) |
| C100 | C99 | C98 | 121.3(12) |
| C101 | C100 | C99 | 119.9(11) |
| C100 | C101 | C102 | 121.7(13) |
| C101 | C102 | C97 | 117.7(11) |
| C104 | C103 | P6 | 124.4(7) |
| C108 | C103 | P6 | 117.3(7) |
| C108 | C103 | C104 | 118.1(9) |
| C105 | C104 | C103 | 120.9(10) |
| C104 | C105 | C106 | 121.0(10) |
| C107 | C106 | C105 | 119.5(10) |
| C106 | C107 | C108 | 120.3(9) |
| C103 | C108 | C107 | 120.2(9) |
| O7 | P7 | C109 | 111.4(4) |
| O7 | P7 | C115 | 114.0(4) |
| O7 | P7 | C121 | 110.4(6) |
| C109 | P7 | C121 | 107.2(5) |
| C115 | P7 | C109 | 108.5(6) |
| C115 | P7 | C121 | 105.0(7) |
| C110 | C109 | P7 | 117.4(8) |
| C110 | C109 | C114 | 119.6(10) |
| C114 | C109 | P7 | 123.1(9) |
| C109 | C110 | C111 | 119.6(10) |
| C112 | C111 | C110 | 120.9(11) |
| C111 | C112 | C113 | 120.8(12) |
| C112 | C113 | C114 | 118.5(14) |
| C109 | C114 | C113 | 120.5(13) |
| C116 | C115 | P7 | 118.9(12) |
| C120 | C115 | P7 | 120.2(14) |
| C120 | C115 | C116 | 120.0(14) |
| C115 | C116 | C117 | 118.0(19) |
| C116 | C117 | C118 | 110.8(19) |
| C119 | C118 | C117 | 129.3(17) |
| C120 | C119 | C118 | 112(2) |
| C119 | C120 | C115 | 128(2) |
| C122 | C121 | P7 | 119.3(14) |
| C126 | C121 | P7 | 119.3(9) |
| C126 | C121 | C122 | 121.3(14) |
| C123 | C122 | C121 | 122(2) |
| C124 | C123 | C122 | 118(2) |
| C123 | C124 | C125 | 124.2(18) |
| C126 | C125 | C124 | 113.5(18) |
| C121 | C126 | C125 | 121.2(14) |

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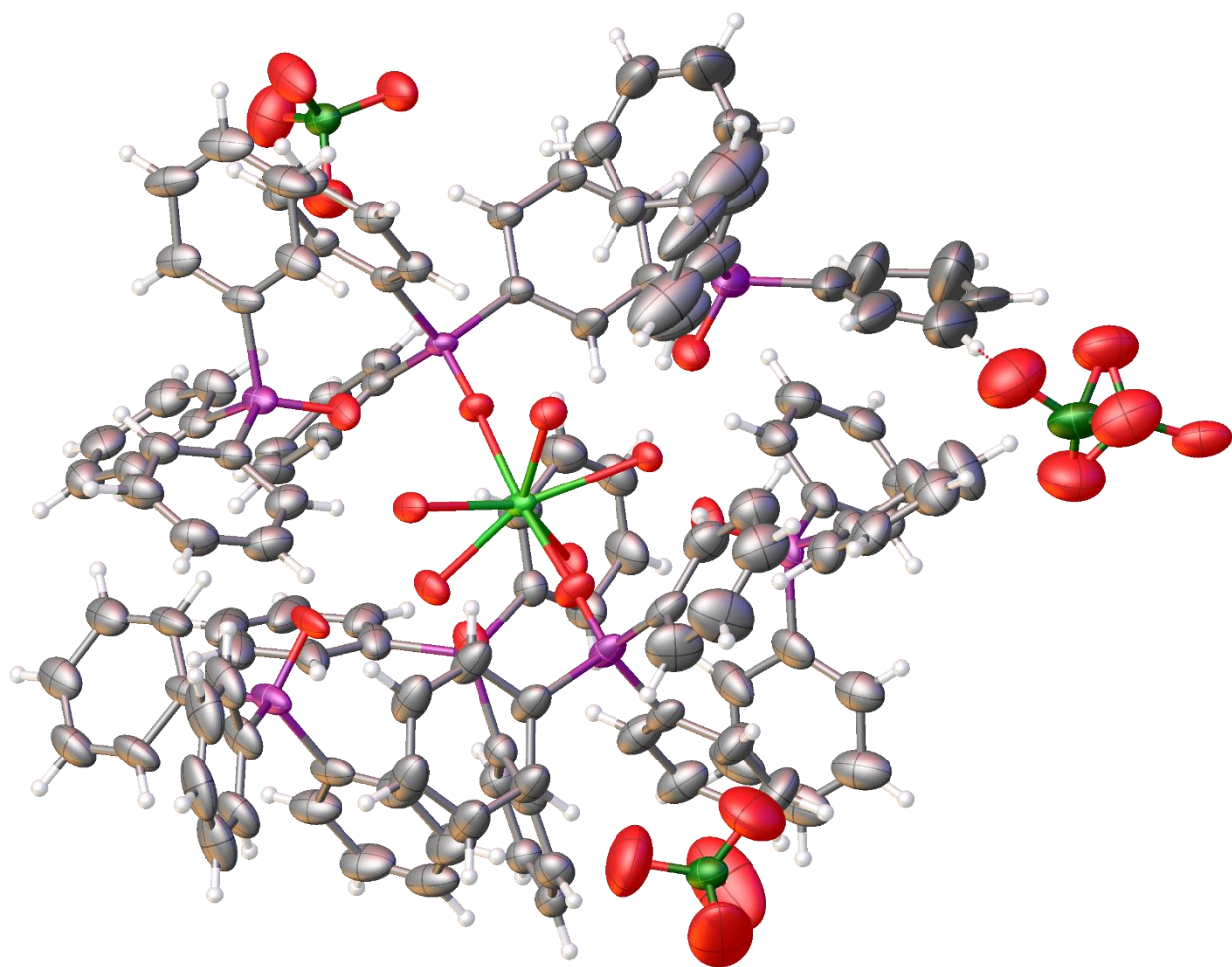
# Crystal Data and Experimental [Nd(k$^3$-O,O,O'- S$_3$O$_6$)(Ph$_3$PO)$_4$(H$_2$O)]·3[ClO$_4$]
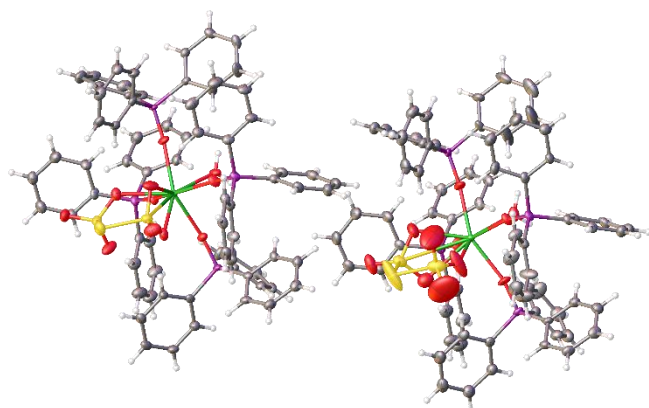


**Figure 1:** Thermal ellipsoids drawn at the 50% probability level.

**Experimental.** A suitable colourless block-shaped crystal (0.300×0.250×0.200 mm$^3$) was selected and mounted on a MITIGEN holder in perfluoroether oil on a Rigaku FRE+ diffractometer equipped with VHF Varimax confocal mirrors and an AFC12 goniometer and HyPix 6000HE detector. The crystal was kept at a steady $T$ = 100(2) K during data collection. The structure was solved with the **ShelXT** (Sheldrick, 2015) structure solution program using the Intrinsic Phasing solution method and by using **Olex2** (Dolomanov et al., 2009) as the graphical interface. The model was refined with version 2014/7 of **ShelXL** (Sheldrick, 2015) using Least Squares minimisation.

**Crystal Data.** C$_{72}$H$_{62}$NdO$_{11}$P$_4$S$_3$, $M_r$ = 1467.51, tetragonal, $P4_3$ (No. 78), a = 19.8658(2) Å, b = 19.8658(2) Å, c = 34.7894(6) Å, $\alpha$ = $\beta$ = $\gamma$ = 90°, $V$ = 13729.6(4) Å$^3$, $T$ = 100(2) K, $Z$ = 8, $Z'$ = 2, $\mu$(MoK$_\alpha$) = 1.000 mm$^{-1}$, 145177 reflections measured, 31470 unique ($R_{int}$ = 0.0395) which were used in all calculations. The final $wR_2$ was 0.1438 (all data) and $R_1$ was 0.0550 (I > 2(I)).

| Formula | C$_{72}$H$_{62}$NdO$_{11}$P$_4$S$_3$ |
|---|---|
| $D_{calc.}$/ g cm$^{-3}$ | 1.420 |
| $\mu$/mm$^{-1}$ | 1.000 |
| Formula Weight | 1467.51 |
| Colour | colourless |
| Shape | block |
| Size/mm$^3$ | 0.300×0.250×0.200 |
| $T$/K | 100(2) |
| Crystal System | tetragonal |
| Flack Parameter | 0.338(12) |
| Hooft Parameter | 0.362(2) |
| Space Group | $P4_3$ |
| a/Å | 19.8658(2) |
| b/Å | 19.8658(2) |
| c/Å | 34.7894(6) |
| $\alpha$/° | 90 |
| $\beta$/° | 90 |
| $\gamma$/° | 90 |
| V/Å$^3$ | 13729.6(4) |
| Z | 8 |
| Z' | 2 |
| Wavelength/Å | 0.71075 |
| Radiation type | MoK$_\alpha$ |
| $\Theta_{min}$/° | 1.556 |
| $\Theta_{max}$/° | 27.483 |
| Measured Refl. | 145177 |
| Independent Refl. | 31470 |
| Reflections with I > 2(I) | 28997 |
| $R_{int}$ | 0.0395 |
| Parameters | 1632 |
| Restraints | 1375 |
| Largest Peak | 3.812 |
| Deepest Hole | -1.784 |
| GooF | 1.038 |
| $wR_2$ (all data) | 0.1438 |
| $wR_2$ | 0.1414 |
| $R_1$ (all data) | 0.0590 |
| $R_1$ | 0.0550 |

## Structure Quality Indicators

**Reflections:**

| d min (Mo) | I/σ | Rint | complete 100% (IUCr) |
|---|---|---|---|
| 0.77 | 31.6 | 3.95% | 100% |

**Refinement:**

| Shift | Max Peak | Min Peak | GooF |
|---|---|---|---|
| -0.002 | 3.8 | -1.8 | 1.038 |

A colourless block-shaped crystal with dimensions 0.300×0.250×0.200 mm$^3$ was mounted on a MITIGEN holder in perfluoroether oil. Data were collected using a Rigaku FRE+ diffractometer equipped with VHF Varimax confocal mirrors and an AFC12 goniometer and HyPix 6000HE detector, and equipped with an Oxford Cryosystems low-temperature device operating at $T$ = 100(2) K.

Data were measured using $\omega$ scans of 0.5 ° per frame for 0.5 s using MoK$_\alpha$ radiation. The total number of runs and images was based on the strategy calculation from the program **CrysAlisPro** (Rigaku, V1.171.40.39a, 2019). The maximum resolution that was achieved was $\Theta$ = 27.483° (0.77 Å).

The diffraction pattern was indexed and the unit cell was refined using **CrysAlisPro** (Rigaku, V1.171.40.39a, 2019) on 49914 reflections, 34% of the observed reflections.

Data reduction, scaling and absorption corrections were performed using **CrysAlisPro** (Rigaku, V1.171.40.39a, 2019). The final completeness is 99.90 % out to 27.483° in $\Theta$.

A multi-scan absorption correction was performed using CrysAlisPro 1.171.40.39a (Rigaku Oxford Diffraction, 2019) using spherical harmonics as implemented in SCALE3 ABSPACK. The absorption coefficient $\mu$ of this material is 1.000 mm$^{-1}$ at this wavelength ($\lambda$ = 0.71075 Å) and the minimum and maximum transmissions are 0.815 and 1.000.

The structure was solved and the space group $P4_3$ (# 78) determined by the **ShelXT** (Sheldrick, 2015) structure solution program using Intrinsic Phasing and refined by Least Squares using version 2014/7 of **ShelXL** (Sheldrick, 2015). All non-hydrogen atoms were refined anisotropically, apart from the two Nd atoms, which were refined isotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. There are some cavities available for solvents (532 and 600 Å$^3$). No solvents were identified and the structure was SQUEEZEd.

*_refine_special_details*:  Refined as a 2-component inversion twin.

The value of Z' is 2. This means that there are two independent molecules in the asymmetric unit.

The Flack parameter was refined to 0.338(12). Determination of absolute structure using Bayesian statistics on Bijvoet differences using the Olex2 results in 0.362(2). Note: The Flack parameter is used to determine chirality of the crystal studied, the value should be near 0, a value of 1 means that the stereochemistry is wrong and the model should be inverted. A value of 0.5 means that the crystal consists of a racemic mixture of the two enantiomers.

## Reflection Statistics

| | | | |
|---|---|---|---|
| Total reflections (after filtering) | 145281 | Unique reflections | 31470 |
| Completeness | 0.999 | Mean $I/\sigma$ | 19.46 |
| $hkl_{max}$ collected | (24, 25, 45) | $hkl_{min}$ collected | (-25, -19, -45) |
| $hkl_{max}$ used | (18, 25, 45) | $hkl_{min}$ used | (-17, 0, -45) |
| Lim $d_{max}$ collected | 100.0 | Lim $d_{min}$ collected | 0.36 |
| $d_{max}$ used | 13.09 | $d_{min}$ used | 0.77 |
| Friedel pairs | 20730 | Friedel pairs merged | 0 |
| Inconsistent equivalents | 83 | $R_{int}$ | 0.0395 |
| $R_{sigma}$ | 0.0316 | Intensity transformed | 0 |
| Omitted reflections | 0 | Omitted by user (OMIT hkl) | 11 |
| Multiplicity | (38200, 32603, 9231, 2152, 651, 194, 165) | Maximum multiplicity | 17 |
| Removed systematic absences | 93 | Filtered off (Shel/OMIT) | 0 |

**Table 1**: Bond Lengths in Å

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|------|------|----------|------|------|----------|
| Nd1 | S1 | 3.2607(18) | C27 | C28 | 1.393(10) |
| Nd1 | O1 | 2.534(5) | C28 | C29 | 1.368(11) |
| Nd1 | O2 | 2.840(7) | C29 | C30 | 1.379(11) |
| Nd1 | O6 | 2.499(5) | C31 | C32 | 1.401(10) |
| Nd1 | O7 | 2.360(5) | C31 | C36 | 1.381(10) |
| Nd1 | O8 | 2.353(5) | C32 | C33 | 1.380(11) |
| Nd1 | O9 | 2.365(5) | C33 | C34 | 1.401(12) |
| Nd1 | O10 | 2.371(5) | C34 | C35 | 1.390(11) |
| Nd1 | O11 | 2.478(6) | C35 | C36 | 1.393(10) |
| S1 | S2 | 2.102(3) | C37 | C38 | 1.394(11) |
| S1 | O1 | 1.475(5) | C37 | C42 | 1.385(10) |
| S1 | O2 | 1.452(6) | C38 | C39 | 1.387(10) |
| S1 | O3 | 1.414(6) | C39 | C40 | 1.363(13) |
| S2 | S3 | 2.144(3) | C40 | C41 | 1.367(13) |
| S3 | O4 | 1.411(6) | C41 | C42 | 1.391(10) |
| S3 | O5 | 1.440(6) | C43 | C44 | 1.386(10) |
| S3 | O6 | 1.442(5) | C43 | C48 | 1.416(10) |
| P1 | O7 | 1.498(5) | C44 | C45 | 1.396(11) |
| P1 | C1 | 1.797(7) | C45 | C46 | 1.391(12) |
| P1 | C7 | 1.786(7) | C46 | C47 | 1.411(12) |
| P1 | C13 | 1.797(8) | C47 | C48 | 1.377(11) |
| P2 | O8 | 1.502(5) | C49 | C50 | 1.406(10) |
| P2 | C19 | 1.791(7) | C49 | C54 | 1.370(9) |
| P2 | C25 | 1.814(7) | C50 | C51 | 1.388(10) |
| P2 | C31 | 1.789(7) | C51 | C52 | 1.379(11) |
| P3 | O9 | 1.502(5) | C52 | C53 | 1.396(11) |
| P3 | C37 | 1.795(7) | C53 | C54 | 1.396(10) |
| P3 | C43 | 1.789(8) | C55 | C56 | 1.399(9) |
| P3 | C49 | 1.798(7) | C55 | C60 | 1.402(9) |
| P4 | O10 | 1.498(5) | C56 | C57 | 1.384(10) |
| P4 | C55 | 1.794(7) | C57 | C58 | 1.385(11) |
| P4 | C61 | 1.797(7) | C58 | C59 | 1.385(11) |
| P4 | C67 | 1.803(7) | C59 | C60 | 1.386(10) |
| C1 | C2 | 1.385(11) | C61 | C62 | 1.396(10) |
| C1 | C6 | 1.391(10) | C61 | C66 | 1.388(10) |
| C2 | C3 | 1.392(11) | C62 | C63 | 1.385(10) |
| C3 | C4 | 1.376(12) | C63 | C64 | 1.380(11) |
| C4 | C5 | 1.343(13) | C64 | C65 | 1.372(11) |
| C5 | C6 | 1.407(10) | C65 | C66 | 1.397(10) |
| C7 | C8 | 1.369(10) | C67 | C68 | 1.397(9) |
| C7 | C12 | 1.410(10) | C67 | C72 | 1.375(10) |
| C8 | C9 | 1.391(10) | C68 | C69 | 1.387(9) |
| C9 | C10 | 1.396(11) | C69 | C70 | 1.390(11) |
| C10 | C11 | 1.379(11) | C70 | C71 | 1.368(11) |
| C11 | C12 | 1.372(11) | C71 | C72 | 1.405(10) |
| C13 | C14 | 1.409(10) | Nd2 | S6 | 3.243(2) |
| C13 | C18 | 1.386(10) | Nd2 | O12 | 2.431(7) |
| C14 | C15 | 1.397(11) | Nd2 | O16 | 2.538(6) |
| C15 | C16 | 1.390(12) | Nd2 | O17 | 2.692(7) |
| C16 | C17 | 1.373(11) | Nd2 | O18 | 2.358(5) |
| C17 | C18 | 1.393(11) | Nd2 | O19 | 2.332(5) |
| C19 | C20 | 1.395(10) | Nd2 | O20 | 2.368(5) |
| C19 | C24 | 1.406(10) | Nd2 | O21 | 2.360(5) |
| C20 | C21 | 1.383(9) | Nd2 | O22 | 2.542(6) |
| C21 | C22 | 1.410(13) | S4 | S5 | 2.151(4) |
| C22 | C23 | 1.379(12) | S4 | O12 | 1.415(8) |
| C23 | C24 | 1.388(10) | S4 | O13 | 1.382(11) |
| C25 | C26 | 1.384(9) | S4 | O14 | 1.373(12) |
| C25 | C30 | 1.386(10) | S5 | S6 | 2.076(4) |
| C26 | C27 | 1.383(10) | S6 | O15 | 1.402(7) |

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|------|------|----------|------|------|----------|
| S6 | O16 | 1.453(6) | C99 | C100 | 1.382(16) |
| S6 | O17 | 1.484(7) | C100 | C101 | 1.377(18) |
| P5 | O18 | 1.500(5) | C101 | C102 | 1.351(15) |
| P5 | C73 | 1.786(7) | C103 | C104 | 1.399(10) |
| P5 | C79 | 1.793(7) | C103 | C108 | 1.389(11) |
| P5 | C85 | 1.803(7) | C104 | C105 | 1.398(11) |
| P6 | O19 | 1.514(5) | C105 | C106 | 1.385(12) |
| P6 | C91 | 1.795(8) | C106 | C107 | 1.359(13) |
| P6 | C97 | 1.790(7) | C107 | C108 | 1.383(12) |
| P6 | C103 | 1.797(8) | C109 | C110 | 1.399(10) |
| P7 | O20 | 1.502(5) | C109 | C114 | 1.389(9) |
| P7 | C109 | 1.809(8) | C110 | C111 | 1.376(11) |
| P7 | C115 | 1.779(7) | C111 | C112 | 1.412(12) |
| P7 | C121 | 1.784(7) | C112 | C113 | 1.383(11) |
| P8 | O21 | 1.495(5) | C113 | C114 | 1.391(10) |
| P8 | C127 | 1.800(7) | C115 | C116 | 1.399(10) |
| P8 | C133 | 1.797(7) | C115 | C120 | 1.417(9) |
| P8 | C139 | 1.795(8) | C116 | C117 | 1.392(10) |
| C73 | C74 | 1.405(11) | C117 | C118 | 1.395(11) |
| C73 | C78 | 1.394(10) | C118 | C119 | 1.398(11) |
| C74 | C75 | 1.391(11) | C119 | C120 | 1.369(10) |
| C75 | C76 | 1.373(13) | C121 | C122 | 1.383(10) |
| C76 | C77 | 1.387(12) | C121 | C126 | 1.387(10) |
| C77 | C78 | 1.387(11) | C122 | C123 | 1.378(12) |
| C79 | C80 | 1.381(10) | C123 | C124 | 1.376(13) |
| C79 | C84 | 1.385(10) | C124 | C125 | 1.375(13) |
| C80 | C81 | 1.394(11) | C125 | C126 | 1.385(11) |
| C81 | C82 | 1.354(12) | C127 | C128 | 1.406(10) |
| C82 | C83 | 1.389(11) | C127 | C132 | 1.388(9) |
| C83 | C84 | 1.386(11) | C128 | C129 | 1.380(10) |
| C85 | C86 | 1.397(9) | C129 | C130 | 1.391(11) |
| C85 | C90 | 1.379(10) | C130 | C131 | 1.387(12) |
| C86 | C87 | 1.401(10) | C131 | C132 | 1.394(10) |
| C87 | C88 | 1.406(10) | C133 | C134 | 1.383(10) |
| C88 | C89 | 1.402(11) | C133 | C138 | 1.409(10) |
| C89 | C90 | 1.395(10) | C134 | C135 | 1.377(11) |
| C91 | C92 | 1.387(10) | C135 | C136 | 1.399(12) |
| C91 | C96 | 1.400(11) | C136 | C137 | 1.401(13) |
| C92 | C93 | 1.393(10) | C137 | C138 | 1.378(12) |
| C93 | C94 | 1.372(12) | C139 | C140 | 1.400(10) |
| C94 | C95 | 1.380(12) | C139 | C144 | 1.377(11) |
| C95 | C96 | 1.390(11) | C140 | C141 | 1.387(11) |
| C97 | C98 | 1.373(10) | C141 | C142 | 1.364(13) |
| C97 | C102 | 1.381(12) | C142 | C143 | 1.386(13) |
| C98 | C99 | 1.384(11) | C143 | C144 | 1.366(12) |

**Table 2**: Bond Angles in °.

| Atom | Atom | Atom | Angle/° |
|------|------|------|---------|
| O1 | Nd1 | S1 | 25.80(12) |
| O1 | Nd1 | O2 | 51.56(16) |
| O2 | Nd1 | S1 | 26.41(11) |
| O6 | Nd1 | S1 | 64.23(12) |
| O6 | Nd1 | O1 | 76.15(17) |
| O6 | Nd1 | O2 | 64.69(17) |
| O7 | Nd1 | S1 | 130.54(13) |
| O7 | Nd1 | O1 | 121.23(17) |
| O7 | Nd1 | O2 | 138.25(17) |
| O7 | Nd1 | O6 | 73.64(17) |
| O7 | Nd1 | O9 | 150.86(19) |
| O7 | Nd1 | O10 | 81.10(17) |
| O7 | Nd1 | O11 | 76.09(17) |
| O8 | Nd1 | S1 | 108.73(13) |
| O8 | Nd1 | O1 | 134.52(17) |
| O8 | Nd1 | O2 | 83.22(17) |
| O8 | Nd1 | O6 | 80.41(18) |
| O8 | Nd1 | O7 | 87.61(18) |
| O8 | Nd1 | O9 | 87.64(18) |
| O8 | Nd1 | O10 | 149.31(18) |
| O8 | Nd1 | O11 | 74.69(16) |
| O9 | Nd1 | S1 | 78.00(13) |
| O9 | Nd1 | O1 | 81.32(17) |
| O9 | Nd1 | O2 | 69.44(18) |
| O9 | Nd1 | O6 | 133.57(17) |
| O9 | Nd1 | O10 | 88.55(18) |
| O9 | Nd1 | O11 | 74.92(17) |
| O10 | Nd1 | S1 | 100.19(12) |
| O10 | Nd1 | O1 | 74.68(17) |
| O10 | Nd1 | O2 | 123.50(17) |
| O10 | Nd1 | O6 | 122.62(17) |
| O10 | Nd1 | O11 | 74.92(16) |
| O11 | Nd1 | S1 | 152.56(12) |
| O11 | Nd1 | O1 | 141.54(16) |
| O11 | Nd1 | O2 | 138.53(16) |
| O11 | Nd1 | O6 | 141.26(17) |
| S2 | S1 | Nd1 | 106.60(9) |
| O1 | S1 | Nd1 | 48.4(2) |
| O1 | S1 | S2 | 106.1(2) |
| O2 | S1 | Nd1 | 60.4(3) |
| O2 | S1 | S2 | 106.9(3) |
| O2 | S1 | O1 | 107.0(4) |
| O3 | S1 | Nd1 | 149.0(3) |
| O3 | S1 | S2 | 103.5(3) |
| O3 | S1 | O1 | 115.5(3) |
| O3 | S1 | O2 | 116.9(4) |
| S1 | S2 | S3 | 100.04(12) |
| O4 | S3 | S2 | 103.0(3) |
| O4 | S3 | O5 | 115.8(4) |
| O4 | S3 | O6 | 114.9(3) |
| O5 | S3 | S2 | 106.1(3) |
| O5 | S3 | O6 | 112.0(4) |
| O6 | S3 | S2 | 103.3(2) |
| O7 | P1 | C1 | 109.7(3) |
| O7 | P1 | C7 | 114.2(3) |
| O7 | P1 | C13 | 109.9(3) |
| C1 | P1 | C13 | 109.0(3) |
| C7 | P1 | C1 | 108.6(3) |
| C7 | P1 | C13 | 105.2(4) |
| O8 | P2 | C19 | 113.0(3) |

| Atom | Atom | Atom | Angle/° |
|------|------|------|---------|
| O8 | P2 | C25 | 111.6(3) |
| O8 | P2 | C31 | 110.2(3) |
| C19 | P2 | C25 | 106.4(3) |
| C31 | P2 | C19 | 108.1(3) |
| C31 | P2 | C25 | 107.3(3) |
| O9 | P3 | C37 | 110.6(3) |
| O9 | P3 | C43 | 109.9(3) |
| O9 | P3 | C49 | 112.8(3) |
| C37 | P3 | C49 | 108.0(3) |
| C43 | P3 | C37 | 109.3(3) |
| C43 | P3 | C49 | 106.1(3) |
| O10 | P4 | C55 | 112.0(3) |
| O10 | P4 | C61 | 111.8(3) |
| O10 | P4 | C67 | 111.3(3) |
| C55 | P4 | C61 | 109.0(3) |
| C55 | P4 | C67 | 106.9(3) |
| C61 | P4 | C67 | 105.6(3) |
| S1 | O1 | Nd1 | 105.8(3) |
| S1 | O2 | Nd1 | 93.2(3) |
| S3 | O6 | Nd1 | 127.4(3) |
| P1 | O7 | Nd1 | 167.6(3) |
| P2 | O8 | Nd1 | 169.9(3) |
| P3 | O9 | Nd1 | 166.9(3) |
| P4 | O10 | Nd1 | 170.3(3) |
| C2 | C1 | P1 | 118.3(6) |
| C2 | C1 | C6 | 120.2(7) |
| C6 | C1 | P1 | 121.3(6) |
| C1 | C2 | C3 | 119.0(7) |
| C4 | C3 | C2 | 120.9(8) |
| C5 | C4 | C3 | 120.2(8) |
| C4 | C5 | C6 | 121.0(8) |
| C1 | C6 | C5 | 118.8(7) |
| C8 | C7 | P1 | 123.6(6) |
| C8 | C7 | C12 | 118.8(7) |
| C12 | C7 | P1 | 117.6(5) |
| C7 | C8 | C9 | 121.5(7) |
| C8 | C9 | C10 | 119.0(7) |
| C11 | C10 | C9 | 119.8(7) |
| C12 | C11 | C10 | 120.8(7) |
| C11 | C12 | C7 | 120.0(7) |
| C14 | C13 | P1 | 121.3(6) |
| C18 | C13 | P1 | 119.6(6) |
| C18 | C13 | C14 | 119.1(7) |
| C15 | C14 | C13 | 120.1(7) |
| C16 | C15 | C14 | 119.5(8) |
| C17 | C16 | C15 | 120.7(8) |
| C16 | C17 | C18 | 120.2(7) |
| C13 | C18 | C17 | 120.4(7) |
| C20 | C19 | P2 | 121.9(5) |
| C20 | C19 | C24 | 120.1(6) |
| C24 | C19 | P2 | 118.0(5) |
| C21 | C20 | C19 | 120.2(8) |
| C20 | C21 | C22 | 119.4(8) |
| C23 | C22 | C21 | 120.5(7) |
| C22 | C23 | C24 | 120.3(8) |
| C23 | C24 | C19 | 119.5(7) |
| C26 | C25 | P2 | 121.8(5) |
| C26 | C25 | C30 | 119.5(7) |
| C30 | C25 | P2 | 118.7(5) |
| C27 | C26 | C25 | 119.6(6) |
| C26 | C27 | C28 | 120.3(7) |
| C29 | C28 | C27 | 120.0(7) |

| Atom | Atom | Atom | Angle/° |
|------|------|------|---------|
| C28 | C29 | C30 | 119.8(7) |
| C29 | C30 | C25 | 120.9(7) |
| C32 | C31 | P2 | 121.3(6) |
| C36 | C31 | P2 | 118.1(5) |
| C36 | C31 | C32 | 120.6(7) |
| C33 | C32 | C31 | 120.1(7) |
| C32 | C33 | C34 | 118.9(7) |
| C35 | C34 | C33 | 121.2(7) |
| C34 | C35 | C36 | 119.2(7) |
| C31 | C36 | C35 | 119.9(7) |
| C38 | C37 | P3 | 118.1(6) |
| C42 | C37 | P3 | 122.3(6) |
| C42 | C37 | C38 | 119.5(7) |
| C39 | C38 | C37 | 119.5(7) |
| C40 | C39 | C38 | 120.5(8) |
| C39 | C40 | C41 | 120.6(8) |
| C40 | C41 | C42 | 120.1(8) |
| C37 | C42 | C41 | 119.8(8) |
| C44 | C43 | P3 | 119.0(6) |
| C44 | C43 | C48 | 119.6(7) |
| C48 | C43 | P3 | 121.3(6) |
| C43 | C44 | C45 | 120.6(7) |
| C46 | C45 | C44 | 119.8(7) |
| C45 | C46 | C47 | 119.7(7) |
| C48 | C47 | C46 | 120.4(8) |
| C47 | C48 | C43 | 119.8(7) |
| C50 | C49 | P3 | 116.7(5) |
| C54 | C49 | P3 | 122.9(6) |
| C54 | C49 | C50 | 120.3(7) |
| C51 | C50 | C49 | 119.4(7) |
| C52 | C51 | C50 | 119.8(7) |
| C51 | C52 | C53 | 121.1(7) |
| C54 | C53 | C52 | 118.7(7) |
| C49 | C54 | C53 | 120.6(7) |
| C56 | C55 | P4 | 118.2(5) |
| C56 | C55 | C60 | 120.0(6) |
| C60 | C55 | P4 | 121.8(5) |
| C57 | C56 | C55 | 119.5(7) |
| C56 | C57 | C58 | 120.6(7) |
| C59 | C58 | C57 | 119.9(7) |
| C58 | C59 | C60 | 120.7(7) |
| C59 | C60 | C55 | 119.3(7) |
| C62 | C61 | P4 | 121.8(5) |
| C66 | C61 | P4 | 118.7(5) |
| C66 | C61 | C62 | 119.5(6) |
| C63 | C62 | C61 | 120.5(7) |
| C64 | C63 | C62 | 119.3(7) |
| C65 | C64 | C63 | 121.0(7) |
| C64 | C65 | C66 | 120.0(7) |
| C61 | C66 | C65 | 119.6(7) |
| C68 | C67 | P4 | 121.7(5) |
| C72 | C67 | P4 | 119.1(5) |
| C72 | C67 | C68 | 119.1(7) |
| C69 | C68 | C67 | 120.4(7) |
| C68 | C69 | C70 | 119.3(7) |
| C71 | C70 | C69 | 121.2(7) |
| C70 | C71 | C72 | 119.0(7) |
| C67 | C72 | C71 | 120.9(7) |
| O12 | Nd2 | S6 | 64.98(17) |
| O12 | Nd2 | O16 | 74.9(3) |
| O12 | Nd2 | O17 | 67.3(2) |
| O12 | Nd2 | O22 | 144.4(2) |

| Atom | Atom | Atom | Angle/° |
|------|------|------|---------|
| O16 | Nd2 | S6 | 25.58(15) |
| O16 | Nd2 | O17 | 52.0(2) |
| O16 | Nd2 | O22 | 137.4(2) |
| O17 | Nd2 | S6 | 26.97(15) |
| O18 | Nd2 | S6 | 79.72(14) |
| O18 | Nd2 | O12 | 136.8(2) |
| O18 | Nd2 | O16 | 84.0(2) |
| O18 | Nd2 | O17 | 70.0(2) |
| O18 | Nd2 | O20 | 146.80(19) |
| O18 | Nd2 | O21 | 88.75(18) |
| O18 | Nd2 | O22 | 72.71(17) |
| O19 | Nd2 | S6 | 96.39(14) |
| O19 | Nd2 | O12 | 117.6(3) |
| O19 | Nd2 | O16 | 71.2(2) |
| O19 | Nd2 | O17 | 120.2(2) |
| O19 | Nd2 | O18 | 89.1(2) |
| O19 | Nd2 | O20 | 81.40(19) |
| O19 | Nd2 | O21 | 152.5(2) |
| O19 | Nd2 | O22 | 73.3(2) |
| O20 | Nd2 | S6 | 132.76(13) |
| O20 | Nd2 | O12 | 74.4(2) |
| O20 | Nd2 | O16 | 121.9(2) |
| O20 | Nd2 | O17 | 141.46(19) |
| O20 | Nd2 | O22 | 74.09(17) |
| O21 | Nd2 | S6 | 110.15(14) |
| O21 | Nd2 | O12 | 81.4(3) |
| O21 | Nd2 | O16 | 135.7(2) |
| O21 | Nd2 | O17 | 84.5(2) |
| O21 | Nd2 | O20 | 85.51(18) |
| O21 | Nd2 | O22 | 80.0(2) |
| O22 | Nd2 | S6 | 150.50(11) |
| O22 | Nd2 | O17 | 139.7(2) |
| O12 | S4 | S5 | 107.3(3) |
| O13 | S4 | S5 | 102.5(5) |
| O13 | S4 | O12 | 108.9(8) |
| O14 | S4 | S5 | 110.2(8) |
| O14 | S4 | O12 | 112.3(8) |
| O14 | S4 | O13 | 114.8(10) |
| S6 | S5 | S4 | 101.89(16) |
| S5 | S6 | Nd2 | 108.56(12) |
| O15 | S6 | Nd2 | 147.3(3) |
| O15 | S6 | S5 | 103.9(3) |
| O15 | S6 | O16 | 116.9(4) |
| O15 | S6 | O17 | 117.4(4) |
| O16 | S6 | Nd2 | 49.0(3) |
| O16 | S6 | S5 | 108.3(3) |
| O16 | S6 | O17 | 102.8(4) |
| O17 | S6 | Nd2 | 55.4(3) |
| O17 | S6 | S5 | 107.0(3) |
| O18 | P5 | C73 | 109.6(3) |
| O18 | P5 | C79 | 113.0(3) |
| O18 | P5 | C85 | 110.8(3) |
| C73 | P5 | C79 | 108.1(3) |
| C73 | P5 | C85 | 109.0(3) |
| C79 | P5 | C85 | 106.2(3) |
| O19 | P6 | C91 | 111.3(3) |
| O19 | P6 | C97 | 110.9(4) |
| O19 | P6 | C103 | 111.0(3) |
| C91 | P6 | C103 | 110.3(3) |
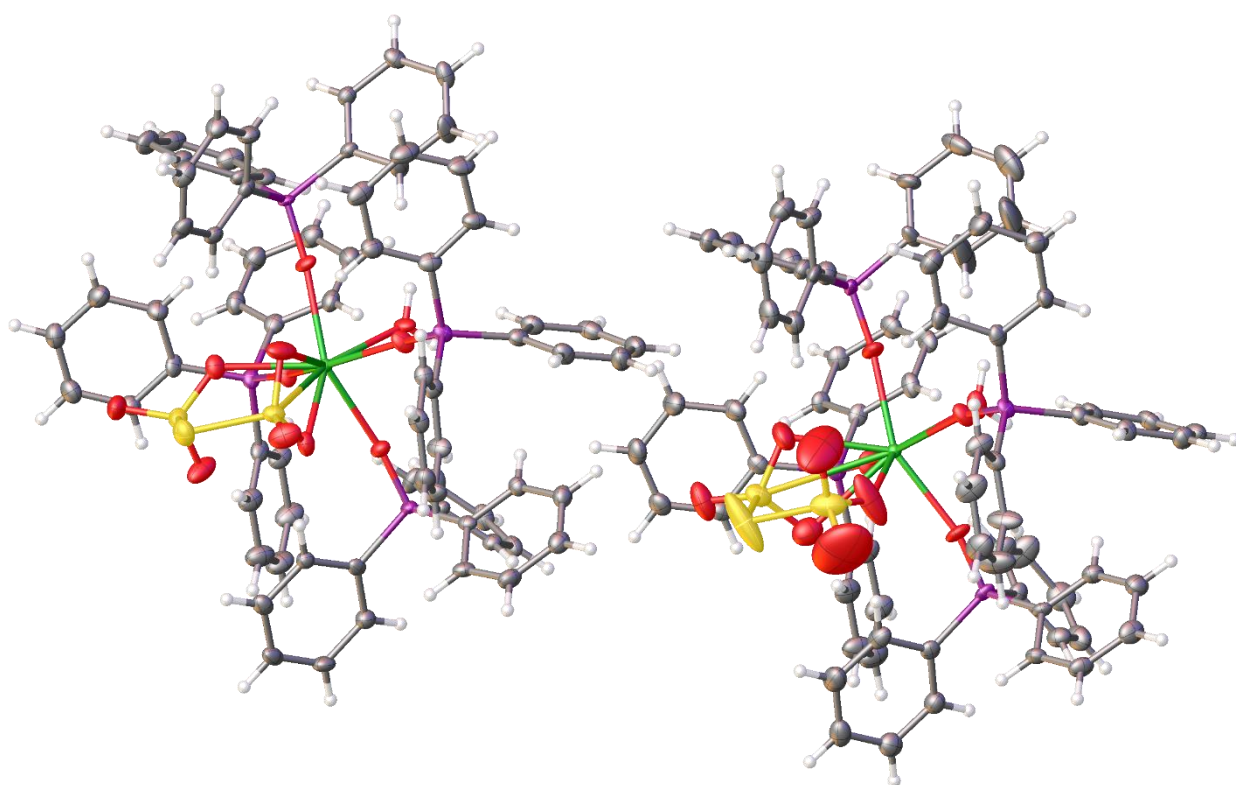
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