

From Parquets to Bricks: A Series of Lanthanide Coordination Polymers with Bis(diphenylphosphino)ethane Dioxide

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A series of new layered coordination polymers consisting of $\text{Ln}[\text{Ph}_2\text{P}(\text{O})\text{--CH}_2\text{CH}_2\text{--P}(\text{O})\text{Ph}_2]_{1.5}$ monomeric units, where $\text{Ln} = \text{Pr}(\text{NO}_3)_3$, $\text{Nd}(\text{NO}_3)_3$, NdCl_3 , $\text{Sm}(\text{NO}_3)_3$, GdCl_3 , $\text{Dy}(\text{NO}_3)_3$, were synthesized and structurally characterized. The majority of prepared compounds display approximately rectangular building blocks. However, the adopted architecture strongly depends on additional nonbridging ligands in the coordination sphere of the cation, as well as on the reaction conditions and the employed solvent. Accordingly, the solvothermally prepared polymers exhibit either parquet-floor or brick-wall architecture, whereas the polymers from gel-diffusion reactions resemble honeycomb networks. The solvothermal reaction of the smallest lanthanide cation Lu^{3+} with $\text{Ph}_2\text{P}(\text{O})\text{--CH}_2\text{CH}_2\text{--P}(\text{O})\text{Ph}_2$ led to a molecular compound instead of a polymer.

Introduction

Bis(diphenylphosphino)ethane and its oxidized derivatives have appeared throughout the coordination chemistry of both transition and main group metals for a few decades.¹ Until now, there are only a few examples of coordination polymers based on the $\text{Ph}_2\text{P}(\text{O})\text{--CH}_2\text{CH}_2\text{--P}(\text{O})\text{Ph}_2$ (dppeO₂) spacer ligand and no systematic work in this area seems to be available.² For a long time, we have been involved in coordination chemistry of P–X–P ligands and studied their coordination capabilities toward selected p-block and d-block elements. Recently we shifted our attention to lanthanides, and while looking for lanthanide chelates, we succeeded in preparing new two-dimensional coordination polymers of praseodymium.³ In our previous communication, we implied that the modification of the $\text{Ph}_2\text{P}(\text{O})\text{--X--P}(\text{O})\text{Ph}_2$ ligand backbone might be attractive for supramolecular design

because an appropriate combination of length and rigidity of the central –X– moiety allows control of the $\text{Ph}_2\text{P}(\text{O})$ donor group separation. The possibility of controlling the porosity of the new materials through the corresponding derivatization of the spacer ligands was always an exciting issue in the development of shape- and size-selective separation and catalysis.⁴ Moreover, there is a potential of replacing the phenyl groups for sterically as well as electronically different substituents. As the area is largely unexplored, we decided to spend some time on a more thorough study, which we mainly devoted to the following aspects: (1) the effect of lanthanide cations and (2) the effect of different reaction conditions on the structure and properties of the resulting polymers.

In the following text, we report the synthesis and structural comparison of a series of 2D coordination polymers of the general formula $\{\text{Ln}(\text{NO}_3)_3[\text{Ph}_2\text{P}(\text{O})\text{--CH}_2\text{CH}_2\text{--P}(\text{O})\text{Ph}_2]_{1.5}\}_n$ ($\text{Ln} = \text{Pr}, \text{Nd}, \text{Sm}, \text{Dy}$). Our attempts to prepare the corresponding compound with lutetium under the same conditions resulted in a molecular compound $\text{Lu}_2(\text{NO}_3)_6\text{--}[\text{Ph}_2\text{P}(\text{O})\text{--CH}_2\text{CH}_2\text{--P}(\text{O})\text{Ph}_2]_3$. To examine the importance of the ancillary ligands in the coordination sphere of the cation, $\{\text{LnCl}_3[\text{Ph}_2\text{P}(\text{O})\text{--CH}_2\text{CH}_2\text{--P}(\text{O})\text{Ph}_2]_{1.5}\}_n$ ($\text{Ln} = \text{Nd}, \text{Gd}$) were also prepared. Because of a low solubility of the

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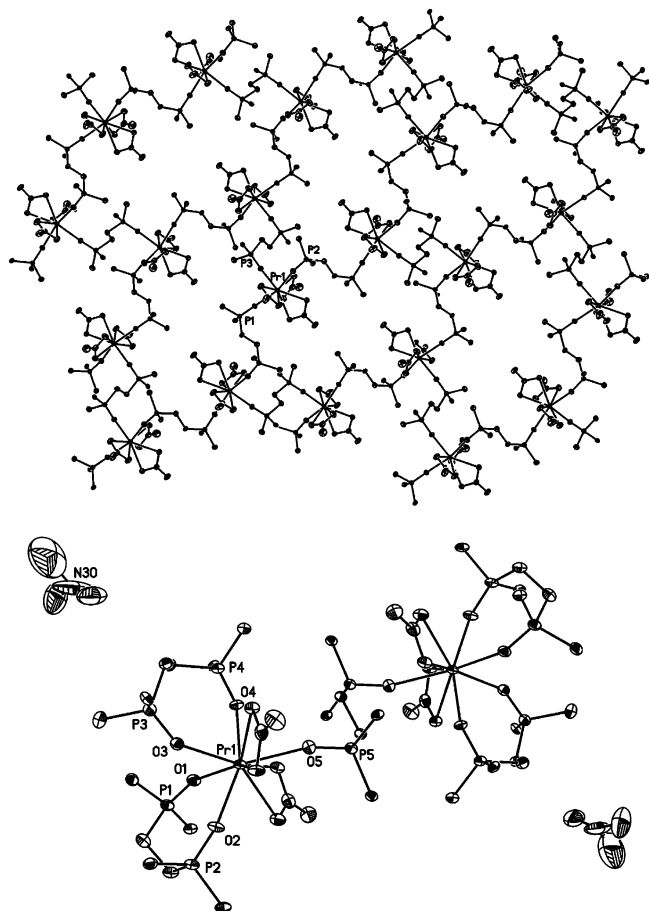


Figure 1. The structures of coordination polymer $[\text{Pr}(\text{NO}_3)_3(\text{dppeO}_2)_{1.5}]_n$ (**1**, top) and binuclear complex $[\text{Pr}_2(\text{NO}_3)_4(\text{dppeO}_2)_5](\text{NO}_3)_2$ (**8**, bottom), prepared by the diffusion of methanolic solutions of $\text{Pr}(\text{NO}_3)_3$ and dppeO_2 .

polymeric compounds, we have focused on the crystallographic characterization of the prepared complexes, although molecular spectroscopy and thermogravimetric analysis were also employed.

Results and Discussion

The initial attempts to prepare the complexes of praseodymium with the dppeO_2 ligand from the methanolic solution led to precipitates insoluble in common organic solvents. To obtain crystalline solids, we decided to slow down the reaction rate by liquid–liquid diffusion (see Experimental Section). After approximately 2 weeks, two different crops of green crystals were isolated. Crystals of **1** were recovered from the lower part of the crystallization tube, while crystalline **8** was found above the bottleneck. The crystal structure of **1** consists of a two-dimensional network of Pr(III) cations and dppeO_2 ligands in a 1:1.5 molar ratio whereas the structure of **8** is binuclear, with four chelating and one bridging ligand around the Pr(III) centers, in an overall 5:2 stoichiometry (Figure 1). Two dramatically different coordination compounds in one reaction mixture were obviously formed as a result of concentration gradients throughout the diffusion apparatus. In looking for the reproducibility of the syntheses of **1** and **8**, the solvothermal reaction in an autoclave was also tested in both 2:3 and 2:5

molar ratios. By heating the methanolic solution of reactants to 140 °C for 24 h and then leaving to cool to ambient temperature, only crystals of **1** were obtained, regardless of the molar ratio used. The solvothermal synthesis of coordination polymers was also successful for the other members of the lanthanide series, with the exception of lutetium. Prolonged heating times (2–5 days) negatively affected the product purity, probably due to the decomposition of the ligand. Another method tested was diffusion through polyethylenoxide gel. In this case the obtained products were all polymeric, although they differed in the stereochemistry and crystal morphologies.

As should be apparent from the above overview, we employed three synthetic methods, namely, solvothermal synthesis, gel diffusion, and liquid–liquid diffusion. While solvothermal syntheses afforded a series of chemically uniform polymers in acceptable yields, the other two approaches provided alternative products, usually in lower yields and purities. With the exception of the binuclear Pr complex **8**, all prepared compounds, molecular and polymeric, arise from a displacement of inner-sphere water present in lanthanide nitrates by the neutral dppeO_2 ligands. In the case of **8**, two additional dppeO_2 ligands partially displace the NO_3 groups from the Pr centers and form a cationic complex. As already mentioned in our previous communication, the six-membered O–P–CH₂CH₂–P–O ligand skeleton is the first example of an appropriate spacer length allowing the polymer formation. The one-atom short diphosphine dioxide ligands are widely known to yield various chelates.⁵ The polymeric compounds are described below in more detail.

Depending on the anion of the starting lanthanide salt, we obtained polymers of different architectures under the solvothermal conditions. Two distinct classes of compounds were prepared, $[\text{Ln}(\text{NO}_3)_3(\text{dppeO}_2)_{1.5}]_n$ (**1**, **2**, **4**, **6**) with the nine-coordinate lanthanide atom and $[\text{LnCl}_3(\text{dppeO}_2)_{1.5}]_n$ (**3**, **5**) with an octahedral coordination. The most regular structural pattern resulted from the inclusion of lanthanide chlorides as nodes into the network; the building blocks are approximately rectangular in shape, with three dppeO_2 spacer ligands forming a “T” around the lanthanide node, giving thus rise to a typical brick-wall architecture in **3** and **5**. The T-shaped coordination remains unchanged in other polymers; however, the shape of the building blocks and the respective motif undergo a remarkable change. With lighter lanthanide nitrates at the nodes, the tiles lose their regular rectangular shape and the laterally viewed polymeric layers resemble heavily undulating waves. Viewed from the top, the network is close to a herringbone or parquet-floor architecture. The diagonal dimensions of the tiles are defined by Ln–Ln separations of ca. $16 \times 23 \text{ \AA}^2$ for **1** and **2** and $19 \times 22 \text{ \AA}^2$ for **3** and **5**. With $\text{Sm}(\text{NO}_3)_3$ and $\text{Dy}(\text{NO}_3)_3$ nodes, the diagonal Ln–Ln distances converge to ca. $19 \times 19 \text{ \AA}^2$, and

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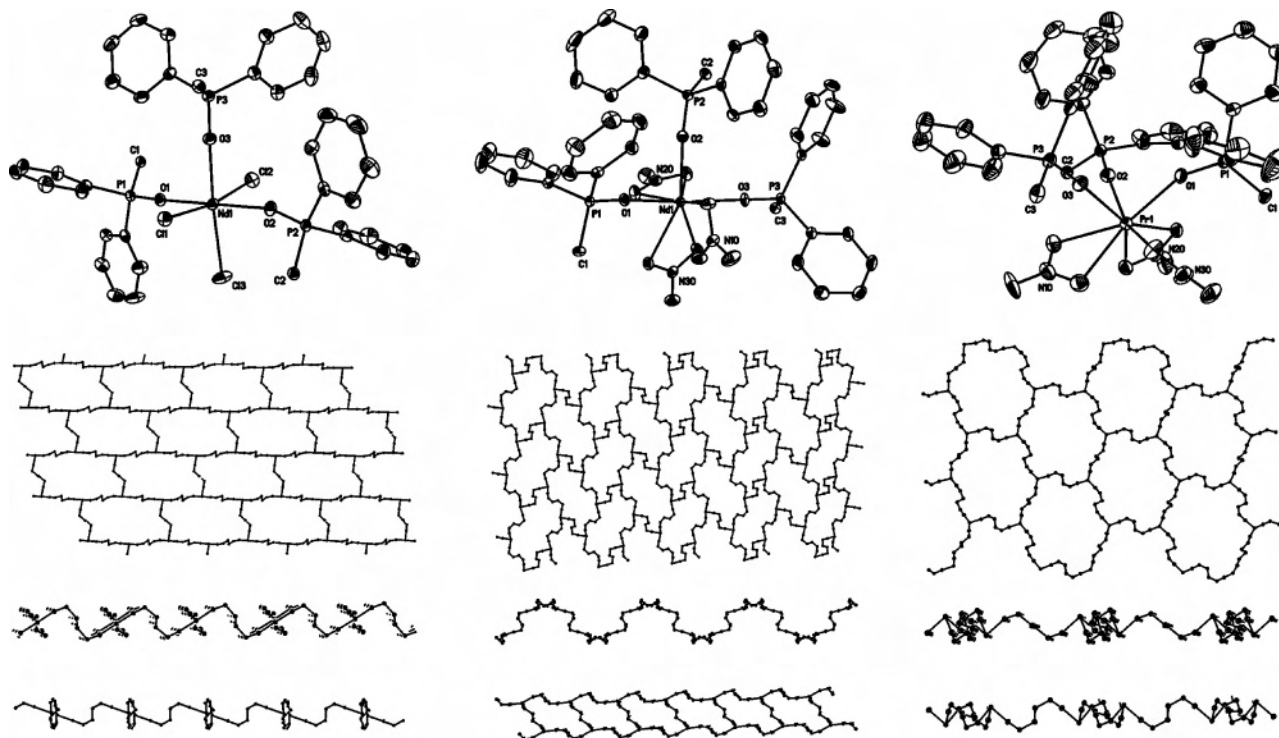


Figure 2. The coordination polyhedra of lanthanide cations, and simplified 2D polymeric layers from top and lateral views in three different polymeric architectures. From left: brick wall (**3**), parquet floor (**2**), and pseudo-honeycomb (**1b**).

thus the building blocks can be considered square-like instead of rectangular. The resulting architecture is then much closer to the brick wall than to the parquet floor obtained with the lighter metals, although the “bricks” are more distorted than in the lanthanide chlorides. The interplanar separations defined as distances of the corresponding atoms in adjacent layers are largest in the chloro complexes, 13.8 Å (**3**) and 13.6 Å (**5**). It is therefore not surprising that the greatest amount of solvent of crystallization was found in these complexes, mainly filling the interplanar space. The stoichiometry was initially refined and later fixed to 1.75 molecules of MeOH per monomeric unit.

The gel-diffusion reaction of $\text{Pr}(\text{NO}_3)_3$ with dppeO_2 afforded crystals of different shapes, with structures belonging to three different space groups. In addition to the crystals of **1** already known from both liquid–liquid diffusion and solvothermal preparation, the majority of the product consisted of hexagonally shaped crystals of **1b** and **1c**. Their hexagonal faces correspond to the almost hexagonal building blocks, which constitute a flatter and more open structure of the $[\text{Pr}(\text{NO}_3)_3(\text{dppeO}_2)_{1.5}]_n$ polymer. The layers are about 11 Å apart, allowing a lot of solvent to be accommodated in the interplanar space. In comparison to **1**, the coordination polyhedron of praseodymium has also changed (Figure 2). The pseudo-octahedral coordination sphere is built of three bidentate NO_3 groups and three oxygen atoms of the dppeO_2 ligands, and these triads are arranged *meridionally* in **1**, while in **1b** and **1c** they form a *facial* isomer. The diffusion through gel media was recently reported to induce the formation of polymorphic coordination polymers, not obtainable by the hydrothermal method.⁶ Our polymers **1** and **1b** (**1c**), and **2** and **2b**, respectively, are additional examples of phases with

different structural properties induced by changing reaction conditions.

Topologically, all presented polymeric networks are of the (6,3) type; however, they span a range of structural motifs. This is enabled by the availability of two different coordination geometries (*fac/mer*) in connection with the conformationally flexible dppeO_2 skeleton. Depending on the reaction conditions, the nature of the lanthanide atom, and the ancillary ligands in its coordination sphere, three main tiling patterns can be distinguished: (1) parquet floor, featuring T-shaped $\text{Ln}(\text{NO}_3)_3$ nodes with lighter Ln atoms, from solvothermal synthesis; (2) brick wall, featuring T-shaped LnCl_3 nodes and $\text{Ln}(\text{NO}_3)_3$ nodes with medium size Ln atoms, from solvothermal synthesis; (3) honeycomb, featuring pyramidal $\text{Ln}(\text{NO}_3)_3$ nodes, from gel diffusion. The latter pattern should be of course considered as a pseudo-honeycomb network, as genuine honeycomb layers are based on trigonal nodes. The presented hexagonal building blocks are only enabled by the flexible P–C–C–P chains, while the nodal geometry is held trigonal pyramidal, with vertexes alternating above and below the middle plane of the hexagons.

In addition to polymeric products, we obtained three examples of molecular compounds. Quite unexpectedly, a binuclear complex $(\text{dppeO}_2)\text{Lu}(\text{NO}_3)_3(\mu\text{-dppeO}_2)\text{Lu}(\text{NO}_3)_3(\text{dppeO}_2)$ (Figure 3) resulted from the solvothermal synthesis in contrast to the coordination polymers formed by other members of the lanthanide series. It is reasonable to think of the small atomic radius of lutetium as being responsible

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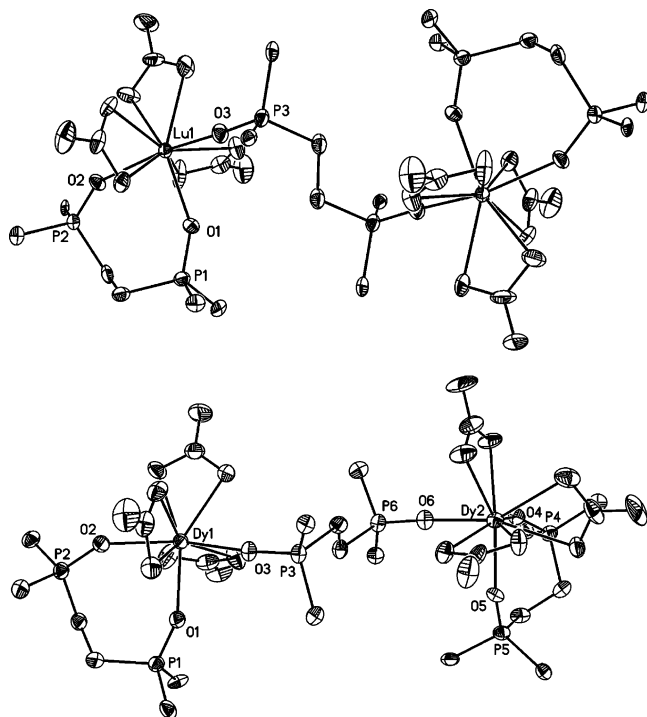


Figure 3. The neutral binuclear complexes $(dppeO_2)Lu(NO_3)_3(\mu-dppeO_2)-Lu(NO_3)_3(dppeO_2)$ (**7**, top) and $(dppeO_2)Dy(NO_3)_3(\mu-dppeO_2)Dy(NO_3)_3(dppeO_2)$ (**9**, bottom).

for the anomaly. Although the coordination number is the same as in the polymeric compounds, the steric congestion exerted by the phenyl substituents on the ligand bridges would be untenable in the polymeric form. Nevertheless, the formation of coordination polymers is not automatically favored for the larger lanthanide nodes. From the liquid–liquid diffusion reaction, an analogous binuclear complex of dysprosium was obtained, $(dppeO_2)Dy(NO_3)_3(\mu-dppeO_2)-Dy(NO_3)_3(dppeO_2)$, while polymeric $[Dy(NO_3)_3(dppeO_2)_{1.5}]_n$ was isolated from the autoclave. This demonstrates the importance of the reaction conditions involved. It is worthwhile to stress the difference between the above-mentioned neutral molecules and the ionic binuclear complex **8** of praseodymium, in which two NO_3^- ligands were displaced by another $dppeO_2$ chelating ligand (Figure 1). As pointed out by Paine et al., the displacement of NO_3^- from the inner coordination sphere of the lanthanide cations is quite uncommon with neutral oxo-donor ligands.⁷ It was observed, however, that the diphosphine dioxide ligands have a propensity to displace the nitrate ions to outer spheres of various chelates.^{5a,7}

All bridging $dppeO_2$ ligands preserve their original anti conformations of donor atoms,⁸ while in the chelating mode they naturally adopt the syn conformation. The corresponding dihedral angles between $O=P-C\dots C-P=O$ planes vary from 155.4 to 180° for the antiparallel (anti) and from 9.2 to 29.8° for parallel (syn) alignments of the $P=O$ groups. The most

important bond lengths and angles are listed in Table 3. In the series of polymers, the $Ln-O(P)$ and $Ln-O(N)$ distances decrease as a function of ionic radius of Ln^{3+} , the distances to the nitrate ligands being about 0.2 \AA longer. The $P=O$ bond distances are very close to the values in the free ligand and are comparable to the $P=O$ distances of $P-X-P$ ligands in related complexes.⁵

The IR spectra show distinct bands at $1468-1492$, $1295-1306$, 1027 , and 817 cm^{-1} suggesting the bidentate chelating nature of the nitrate groups, as previously observed in analogous lanthanide complexes.^{5c,9} We also observe the bands at $1384-1385 \text{ cm}^{-1}$, assigned by Lees to the ionic nitrate formed upon substitution of nitrate ligands by bromide ions in the KBr pellet.^{5c} This band in **8** is relatively more pronounced, thus confirming the ionic nature of the binuclear complex itself. The $P=O$ stretching is displayed as a prominent band in the $1142-1150 \text{ cm}^{-1}$ range and is of course lower in wavenumber than the free $dppeO_2$ (1175 cm^{-1}).^{1a}

The thermal behavior of polymeric compounds **1-6** and the binuclear complex **7** was examined by thermogravimetric methods (TG/DTG/DTA) in the temperature range up to $1000 \text{ }^\circ\text{C}$. The onset temperatures, mass losses, and exo-/endothermic maxima are listed in Table 4 in the Supporting Information. The species containing chloride ligands (**3** and **5**) accommodate in their interlayer space intercalated solvent molecules that are released upon heating to $120-130 \text{ }^\circ\text{C}$. Further raising the temperature causes in all compounds a fast weight loss in two steps. The first event is accompanied with a strong exothermic effect, and this reaction may be assigned to the partial oxidation of organic constituents of the ligands by the nitrate. The decomposition of the NO_3^- ligands is documented by the absence of the nitrate bands in the IR spectrum of compound **7** after being heated to $350 \text{ }^\circ\text{C}$. Furthermore, changing the atmosphere to nitrogen in the TGA experiments with compounds **1-7** had little effect on the position of the onset temperatures and exothermic maxima of the nitrate decomposition. The decomposition temperatures decrease along the lanthanide series which may arise from the polarization effects of the cations on the NO_3^- ligands. The onset temperatures observed for the chloride compounds are about $50-60 \text{ }^\circ\text{C}$ higher than for more labile nitrate counterparts. The end points of these breakdown reactions were found in a remarkably narrow range of $506-527 \text{ }^\circ\text{C}$, and the experimentally determined weight losses correspond well to the complete loss of organic matter (Table 4 in the Supporting Information). The residues obtained after heating the samples to $1000 \text{ }^\circ\text{C}$ were crystalline, and the powder XRD experiments revealed the presence of mixtures of respective ortho and metaphosphates.

Conclusion

This work is the first thorough study on coordination polymers containing $Ph_2P(O)-CH_2CH_2-P(O)Ph_2$ as a spacer

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Table 1. Overview of the Prepared Compounds

lanthanide salt	character of the product	product formula	product number
Solvothermal Synthesis			
Pr(NO ₃) ₃ ·6H ₂ O	polymer, parquet floor	[Pr(NO ₃) ₃ (dppeO ₂) _{1.5}] _n ^a	1
Nd(NO ₃) ₃ ·6H ₂ O	polymer, parquet floor	[Nd(NO ₃) ₃ (dppeO ₂) _{1.5}] _n	2
NdCl ₃ ·6H ₂ O	polymer, brick wall	[NdCl ₃ (dppeO ₂) _{1.5}] _n	3
Sm(NO ₃) ₃ ·6H ₂ O	polymer, brick wall	[Sm(NO ₃) ₃ (dppeO ₂) _{1.5}] _n	4
GdCl ₃ ·6H ₂ O	polymer, brick wall	[GdCl ₃ (dppeO ₂) _{1.5}] _n	5
Dy(NO ₃) ₃ ·6H ₂ O	polymer, brick wall	[Dy(NO ₃) ₃ (dppeO ₂) _{1.5}] _n	6
Lu(NO ₃) ₃ ·2H ₂ O	binuclear	[Lu ₂ (NO ₃) ₆ (dppeO ₂) ₃]	7
Liquid–Liquid Diffusion			
Pr(NO ₃) ₃ ·6H ₂ O	polymer, parquet floor	[Pr(NO ₃) ₃ (dppeO ₂) _{1.5}] _n ^a	1
	binuclear	[Pr ₂ (NO ₃) ₄ (dppeO ₂) ₃](NO ₃) ₂	8
Dy(NO ₃) ₃ ·6H ₂ O	binuclear	[Dy ₂ (NO ₃) ₆ (dppeO ₂) ₃]	9
Gel Diffusion			
Pr(NO ₃) ₃ ·6H ₂ O	polymer, parquet floor	[Pr(NO ₃) ₃ (dppeO ₂) _{1.5}] _n ^a	1
	polymer, honeycomb-like	[Pr(NO ₃) ₃ (dppeO ₂) _{1.5}] _n	1b
	polymer, honeycomb-like	[Pr(NO ₃) ₃ (dppeO ₂) _{1.5}] _n	1c
Nd(NO ₃) ₃ ·6H ₂ O	polymer, honeycomb-like	[Nd(NO ₃) ₃ (dppeO ₂) _{1.5}] _n	2b

^a More details on the structure determination can be found in the Supporting Information to ref 3.

Table 2. Crystal Data and Refinement Parameters

	1b	2	2b	3	4
empirical formula	C ₃₉ H ₃₆ N ₃ O ₁₂ P ₃ Pr·C ₃ Cl ₃	C ₃₉ H ₃₆ N ₃ NdO ₁₂ P ₃	C ₃₉ H ₃₆ N ₃ NdO ₁₂ P ₃ ·C ₃ Cl ₃	C ₃₉ H ₃₆ Cl ₃ NdO ₃ P ₃ ·C _{1.75} O _{1.75}	C ₃₉ H ₃₆ N ₃ O ₁₂ P ₃ Sm·C _{0.25} O _{0.25}
formula weight	1114.91	975.86	1118.24	945.20	988.97
crystal system	triclinic	monoclinic	triclinic	triclinic	triclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> [Å]	12.081(2)	12.981(4)	12.113(1)	13.049(11)	12.113(3)
<i>b</i> [Å]	15.004(2)	20.006(13)	15.015(1)	13.874(11)	16.666(3)
<i>c</i> [Å]	15.599(2)	16.681(5)	15.645(1)	15.028(12)	21.747(5)
α [deg]	114.90(1)	90	114.95(1)	106.09(7)	99.66(2)
β [deg]	90.23(1)	108.29(3)	90.16(1)	96.71(7)	96.48(2)
γ [deg]	109.24(1)	90	109.31(1)	116.24(8)	107.17(2)
volume [Å ³]	2388(1)	4113(3)	2401(1)	2252(3)	4073(1)
<i>Z</i>	2	4	2	2	4
ρ [Mg/m ³]	1.551	1.576	1.547	1.394	1.613
μ [mm ⁻¹]	1.350	1.444	1.409	1.475	1.626
reflns collected/unique	23486/8410	46168/7226	29172/8458	19714/7839	29970/14295
data/parameters	8410/614	7226/524	8458/614	7839/487	14295/1064
final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	0.0320, 0.0603	0.0254, 0.0590	0.0266, 0.0688	0.0264, 0.0737	0.0356, 0.0853
$\Delta\rho_{\max}/\Delta\rho_{\min}$ [e. Å ⁻³]	0.768/−0.393	0.688/−0.695	0.898/−0.606	0.707/−0.669	1.993/−1.350
	5	6	7	8	9
empirical formula	C ₃₉ H ₃₆ Cl ₃ GdO ₃ P ₃ ·C _{1.75} O _{1.75}	C ₃₉ H ₃₆ DyN ₃ O ₁₂ P ₃	C ₃₉ H ₃₆ LuN ₃ O ₁₂ P ₃ ·C _{0.50} O _{0.50}	C ₆₅ H ₆₁ N ₃ O ₁₄ P ₅ Pr·C _{1.50} O _{1.50}	C ₃₉ H ₃₆ DyN ₃ O ₁₂ P ₃ ·CO
formula weight	958.21	994.12	1020.59	1445.94	1022.13
crystal system	triclinic	triclinic	triclinic	triclinic	triclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> [Å]	12.766(3)	14.284(12)	12.781(5)	12.188(1)	10.8632(9)
<i>b</i> [Å]	13.594(3)	14.768(12)	16.527(6)	12.559(2)	19.1127(13)
<i>c</i> [Å]	14.686(3)	19.818(11)	20.306(6)	23.158(3)	21.658(2)
α [deg]	105.79(3)	96.74(6)	77.35(3)	77.29(1)	103.29(1)
β [deg]	96.98(3)	94.47(6)	76.72(3)	88.72(1)	101.75(1)
γ [deg]	115.64(3)	106.69(7)	88.10(3)	68.98(1)	91.69(1)
volume [Å ³]	2125(1)	3949(5)	4073(2)	3222(1)	4271(1)
<i>Z</i>	2	4	4	2	4
ρ [Mg/m ³]	1.497	1.672	1.664	1.491	1.590
μ [mm ⁻¹]	1.902	2.081	2.610	0.951	1.929
reflns collected/unique	18304/7464	25311/13533	32028/14308	27894/11323	45137/15003
data/parameters	7464/496	13533/1045	14308/1064	11323/827	15003/1081
final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	0.0286, 0.0607	0.0420, 0.1029	0.0387, 0.0554	0.0471, 0.0835	0.0475, 0.1129
$\Delta\rho_{\max}/\Delta\rho_{\min}$ [e. Å ⁻³]	0.986/−0.706	1.586/−1.562	1.135/−0.930	1.580/−1.135	1.614/−1.479

ligand. A series of two-dimensional lanthanide coordination polymers possessing LnX₃[dppeO₂]_{1.5} (Ln = Pr, Nd, Sm, Gd, Dy; X = NO₃, Cl) building units was obtained and crystallographically characterized. In addition, three binuclear lanthanide complexes with chelating and bridging dppeO₂ ligands were also prepared. Three synthetic methods were

used, solvothermal, liquid diffusion, and gel diffusion. The following observations are worth noting.

(1) Synthetic Methods. The solvothermal synthesis in methanol was found to be the most suitable for the preparation of highly uniform, crystalline coordination polymers. On the other hand, the other two methods afforded structures

Table 3. Selected Average Bond Lengths (Å) and Angles (deg) for Prepared Compounds and the Parent dppeO₂ Ligand

	dppeO ₂ ^b	1 ^b	1b	2	2b	3	4	5	6	7	8	9
Ln–Cl						2.761		2.667				
Ln–O (to N)		2.583	2.575	2.555	2.563		2.526		2.451	2.437	2.613	2.468
Ln–O (to P)		2.385	2.374	2.374	2.370	2.374	2.334	2.282	2.258	2.236	2.419	2.276
P–O	1.492	1.505	1.510	1.504	1.511	1.529	1.497	1.502	1.486	1.495	1.496	1.499
P–C ^a	1.795	1.806	1.801	1.801	1.809	1.828	1.810	1.804	1.790	1.797	1.799	1.797
Ln–O–P		169.6	166.6	169.4	166.5	171.9	168.2	171.1	164.1	156.1	154.4	156.8
O–P–C ^a	108.6	112.1	111.1	112.2	111.2	111.8	111.4	111.8	111.8	111.8	112.8	112.4

^a C is the carbon atom in the CH₂CH₂ central moiety. ^b The values taken from ref 3.

which would remain undiscovered by the solvothermal approach. The liquid–liquid diffusion yields also the binuclear species, with 3:2 and 5:2 ligand-to-metal ratios. The shape of the polymer framework is sensitive to the solvent and conditions used during the synthesis, as the products from the gel diffusion show more open structures with bulky solvent molecules inserted between the polymeric layers.

(2) Structural Aspects. All polymers prepared by the solvothermal method are based on T-shaped nodes. Depending on the metal Ln and ancillary ligands X present in the LnX₃[dppeO₂]_{1.5} node, the building blocks assemble in either parquet-floor (LnX₃ = Pr(NO₃)₃, Nd(NO₃)₃) or brick-wall (LnX₃ = Sm(NO₃)₃, Dy(NO₃)₃, NdCl₃, GdCl₃) architecture. In the gel diffusion products, the Ln coordination polyhedron has changed to a trigonal pyramid (considering bridging ligands) under the influence of the bulky solvent molecules. Because of the flexible ligand skeleton, the resulting polymer closely resembles a honeycomb network.

(3) Lanthanide Contraction. Most probably as a result of the lanthanide contraction, the solvothermal synthesis was unsuccessful in the preparation of the {Lu(NO₃)₃[dppeO₂]_{1.5}}_n polymer. Apparently the dppeO₂ ligand is too short and flexible to hold the small nodes far apart and avoid repulsive forces between them. Our future research will be focused on the interaction of lanthanide cations with diphosphine dioxide based ligands, modified in their backbones to examine the effects of the spacer length and flexibility.

Experimental Section

Owing to the high stability of fully oxidized ligands and lanthanide salts, all manipulations can be performed without strictly anhydrous conditions. Nevertheless, all solvents used (methanol, dichloromethane) were dried and distilled prior to use. Commercially available 1,2-bis(diphenylphosphino)ethane dissolved in tetrahydrofuran was oxidized by 30% aqueous solution of hydrogen peroxide to give Ph₂P(O)–CH₂CH₂–P(O)Ph₂ (dppeO₂). IR spectra (KBr pellets, 4000–400 cm⁻¹) were collected on an Equinox 55/S/NIR FTIR spectrometer. Thermogravimetric analyses (TG/DTG/DTA) were carried out on a MOM Derivatograph-C instrument under static air or flowing nitrogen with 5°/min ramp to 1000 °C. Microanalyses were performed using a ThermoFinnigen Co. CHN Analyzer Flash EA 1112. Of the three methods described below, only the solvothermal synthesis was considered to lead to uniform new compounds in meaningful yields and reasonable purity, while the other two methods were intended for testing the influence of alternative experimental conditions on the structure of the resulting compounds. Therefore the full analytical and spectroscopic characterization is included for the former, whereas the products of the diffusion methods were solely subjects of X-ray diffraction studies.

Solvothermal Syntheses. In a typical preparation, a mixture of dppeO₂ (250 mg, 0.581 mmol) with half an equivalent of lanthanide salt in methanol (30 mL) was sealed in a 250-mL stainless steel reactor Berghof HR-200 with a Teflon liner, heated under autogenous pressure for 1 day to 140 °C with a RHS-295 heater controlled by a BAR-945 unit, and then slowly cooled to room temperature. After 2 days the crystalline solid was collected and washed with methanol. The experimental details for each of the solvothermally prepared compounds are given below (the data for **1** are in the Supporting Information to ref 3); the key to compound formulas is in Table 1.

(a) 2: Nd(NO₃)₃·6H₂O (127 mg, 0.290 mmol); yield 185 mg (58.8%). Anal. required (found): C 48.00 (47.25); H 3.72 (3.61); N 4.31 (4.02). IR: 3056vw, 2964vw, 2914vw, 1591vw, 1483s, 1438s, 1408w, 1384w, 1295s, 1171m, 1149vs, 1123m, 1091s, 1070w, 1027m, 998w, 817w, 769w, 742s, 735m, 728s, 692m, 552vw, 533s, 510m.

(b) 3: NdCl₃·6H₂O (104 mg, 0.290 mmol); yield 219 mg (75.1%). Anal. required (found): C 52.27 (50.19); H 4.05 (4.12). IR: 3374w, 3054vw, 2940vw, 2903vw, 1628vw, 1591vw, 1485vw, 1438m, 1409vw, 1169w, 1142vs, 1125m, 1089s, 1073w, 1027vw, 998vw, 774w, 746m, 730m, 694m, 553w, 536m, 507w.

(c) 4: Sm(NO₃)₃·6H₂O (129 mg, 0.290 mmol); yield 203 mg (64.1%). Anal. required (found): C 47.70 (47.33); H 3.70 (3.52); N 4.28 (3.91). IR: 3058vw, 2965vw, 2913vw, 1592vw, 1484s, 1438s, 1408w, 1385w, 1298s, 1175m, 1150vs, 1123s, 1094s, 1074w, 1027m, 998w, 817w, 767w, 742s, 729s, 690m, 552vw, 535s, 506m.

(d) 5: GdCl₃·6H₂O (108 mg, 0.291 mmol); yield 227 mg (76.8%). Anal. required (found): C 51.52 (49.11); H 3.99 (3.92). IR: 3360w, 3055vw, 2941vw, 2904vw, 1628vw, 1591vw, 1486vw, 1438m, 1409vw, 1174w, 1145vs, 1126m, 1092s, 1071vw, 1028vw, 998vw, 773w, 745w, 731m, 694w, 553w, 535m, 509w.

(e) 6: Dy(NO₃)₃·6H₂O (133 mg, 0.291 mmol); yield 195 mg (60.8%). Anal. required (found): C 47.12 (47.09); H 3.65 (3.32); N 4.23 (3.75). IR: 3059vw, 2964vw, 2914vw, 1592vw, 1492vw, 1488s, 1484s, 1479s, 1438m, 1408w, 1384m, 1306m, 1150vs, 1124m, 1098m, 1073vw, 1028w, 998vw, 816vw, 767w, 742m, 730m, 690m, 552w, 534m, 506w.

(f) 7: Lu(NO₃)₃·2H₂O (115 mg, 0.290 mmol); yield 153 mg (50.6%). Anal. required (found): C 46.53 (45.71); H 3.61 (3.48); N 4.17 (3.65). IR: 3060vw, 2955vw, 2916vw, 1591vw, 1507m, 1483s, 1439s, 1408w, 1384m, 1312vs, 1182m, 1165vs, 1142s, 1126m, 1101m, 1072vw, 1030m, 998w, 816w, 742s, 735s, 726s, 692m, 676w, 553s, 533m, 506m.

Liquid–Liquid Diffusion. A test tube (length, 140 mm; inner diameter, 17 mm) was constricted in the middle (inner diameter, 3.5 mm); the bottom part was filled with the methanolic solution of a lanthanide salt (0.290 mmol), and the dppeO₂ (0.581 mmol) solution in methanol was placed in the upper part. The crystals of diverse quality were mainly formed at the constriction and in the bottom part of the tube.

Gel Diffusion. The gel medium was prepared by mixing polyethylenoxide (MW = 100.00) (3.0 g) with ethanol (12 mL) and 1,2-dichloroethane (12 mL). Three gel mixtures were then layered in the test tube (from the bottom): the solution of lanthanide salt (0.290 mmol) in gel (9 mL), pure gel (6 mL), and dppeO₂ (0.581 mmol) solution in gel (9 mL). The tube was left standing in vertical position for 2–4 weeks at ambient temperature, until the crystalline solid was formed. The crystals suitable for the single crystal X-ray diffraction experiment were removed from the gel and carefully washed with ethanol.

Crystallography. Diffraction data were collected on a KUMA KM-4 κ -axis diffractometer equipped with a CCD detector, using Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). The temperature during data collection was 120(2) K. The intensity data were corrected for Lorentz and polarization effects; absorption correction was applied for all data. The structures were solved by either direct or heavy atom methods and refined by full-matrix least-squares methods using anisotropic thermal parameters for the non-hydrogen atoms, with few exceptions of disordered solvent molecules. The software packages used were the Xcalibur CCD system for the data collection/reduction¹⁰ and SHELXTL for the structure solution, refinement, and drawing preparation.¹¹ In figures the thermal ellipsoids were drawn at the 50% probability level, hydrogen atoms

were omitted, and phenyl groups were usually reduced to a P-substituted ipso-carbon for clarity. Details of the data collection and structure refinement are listed in Table 2. Because of the considerable disorder in the solvent molecules and low data quality, the refinement of **1c** was not completed at a satisfactory level, and we only give the cell parameters and space group.¹² Nevertheless, the general features of the structure including coordination polyhedron and shape of the polymer are identical to the structure of **1b**.

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Supporting Information Available: X-ray crystallographic data in CIF format; results of thermogravimetric analysis under static air for solvothermally prepared compounds (Table 4). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(10) Xcalibur CCD System, CrysAlis Software System, version 1.170; Oxford Diffraction Ltd.: Oxford, U.K., 2003.

(11) SHELXTL, version 5.10; Bruker AXS Inc.: Madison, WI, 1997.
(12) Monoclinic, space group *Cc*, $a = 27.318(2)$, $b = 15.708(2)$, $c = 21.774(2) \text{ \AA}$, $\beta = 101.74(1)^\circ$, $V = 9148(1) \text{ \AA}^3$.