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The Synthesis and Crystal Structures of Two-Dimensional Coordination Polymers of $Ph_2P(O)–CH_2CH_2–P(O)Ph_2$ and $Ph_2P(O)–C_5H_3N–P(O)Ph_2$ with Praseodymium

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Reactions of $Pr(NO_3)_3$ with $Ph_2P(O)–CH_2CH_2–P(O)Ph_2$ and $Ph_2P(O)–C_5H_3N–P(O)Ph_2$ yielded layered network coordination polymers with bidentate ligands spanning the lanthanide atoms in a bridging fashion. The praseodymium cations with “spacer” ligands form two-dimensional building blocks assembling into either square grid or herringbone network.

Compounds of general formula $Ph_2P(E)-X-P(E)Ph_2$ (X = NH, CH_2, CH_2CH_2; E = O, S) have been widely used as chelating ligands in coordination chemistry for at least two decades.[1] Among them, bearing in mind lanthanide preference for hard donors, P−X−P ligands with $Ph_2P(O)$ groups appear to be the most suitable to coordinate, and many chelate complexes were already reported.[2] Such compounds are of molecular character, at most showing hydrogen bonded networks in the solid phase. In this work, we present coordination polymers, where the bidentate (O)P−X−P(O) ligands undergo a change from chelating to bridging mode.

In contrast to transition metals, the use of lanthanide cations in the construction of coordination polymers is still relatively rare and leads to one-dimensional chains, although some examples of 2D and 3D frameworks already appeared.[3] The lanthanide cations are unique in their large size and propensity to high coordination numbers and, therefore, can be legitimately expected to support formation of more open, and coordinatively unsaturated, structures with anticipated catalytic activity.[3j] In addition to nearly traditional shape- and size-selective separating and catalytic properties based on their porosity, the lanthanide-containing frameworks bring the interesting aspect of luminiscence. The combination of lanthanides with appropriate chromophoric ligands can be exploited to obtain long-lived, highly fluorescent materials.[3g]

Three covalently bonded chain (1D) structures possessing the $R_2P(O)-X-P(O)R_2$ bridging backbone are known;[4] however, there is no crystallographically characterized two-dimensional lanthanide polymer with bridging ligands of diphosphine dioxide type. In the following text, we report the synthesis of 2D coordination polymers of praseodymium with two neutral ligands $Ph_2P(O)-C_5H_3N-P(O)Ph_2$ ($dpppO_2$) and $Ph_2P(O)-CH_2CH_2-P(O)Ph_2$ ($dppeO_2$), that mainly differ in flexibility of their central parts (either pyridine or ethane).

In our experimental work, we used different methods of preparation, including the solvothermal synthesis. Compound **1** was prepared by a slow evaporation of dichloromethane from the solution of ligand and praseodymium(III) nitrate. Mixing $dppeO_2$ and $Pr(NO_3)_3$ in a similar way led to almost immediate precipitation of amorphous **2**; thus, we turned our attention to the solvothermal reaction which yielded after 2 days at 140 °C green crystals of good quality. It should also be noted that our effort to prepare **1** by solvothermal route was unsuccessful in three different solvents (water, methanol,

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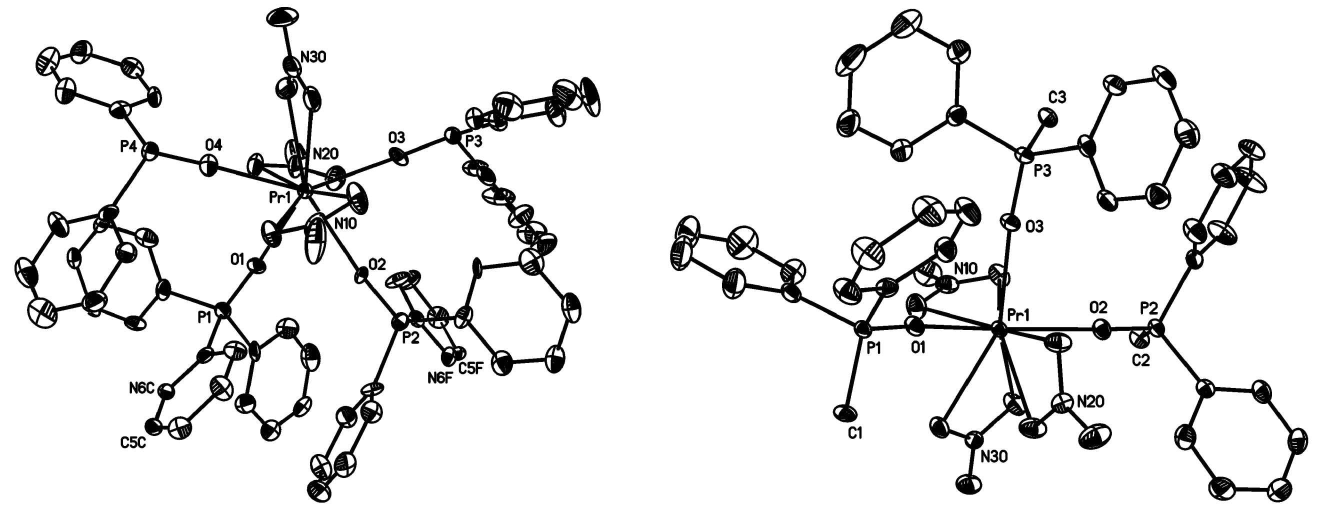

Figure 1. Coordination environments of **1** (left) and **2** (right), where only parts of each $dpppO_2$ and $dppeO_2$ ligands are shown (the other ligand parts are generated by symmetry and connected to atoms labeled as P3, P4, C5C, and C5F (**1**), and C1, C2, and C3 (**2**), respectively). The thermal ellipsoids are drawn at the 50% probability level, and all hydrogen atoms were omitted for clarity.

Scheme 1. Reactants Used in the Preparation of Coordination Polymers

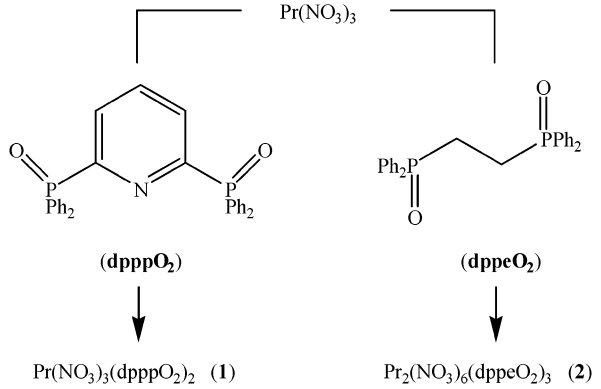

Table 1. Selected Average Bond Lengths [Å] and Angles [deg] for Complexes **1** and **2**, and for the Parent Ligands

	$dpppO_2$	**1**	$dppeO_2$	**2**
Pr−O (to N)		2.657		2.583
Pr−O (to P)		2.482		2.385
P−O	1.479	1.495	1.492	1.505
P−C[a]	1.807	1.831	1.795	1.806
Pr−O−P		170.0		169.6
O−P−C[a]	110.9	110.5	108.6	112.1

[a] C is the carbon atom in either pyridine or ethane central moieties.

dichloromethane). The reaction components are described by Scheme 1.

It is worth mentioning that the 1:2 reaction of $Pr(NO_3)_3$ with the $Ph_2P(O){-}CH_2{-}P(O)Ph_2$ ($dppmO_2$) ligand, one carbon shorter than $dppeO_2$ in its backbone, led to a chelate instead of a chain or a layered structure.[2b] A similar ligand based on $Ph_2P(O){-}CH_2CH_2CH_2{-}P(O)Ph_2$ (modified with pyridine *N*-oxide) forms a chain structure.[4a] It seems that because of the smaller bite angle, $dppmO_2$ is not able to hold the praseodymium centers apart enough without significant repulsion between neighboring ligands. On the other hand, the potentially large bite is by no means sufficient to cause bridging behavior of the ligand, as it was previously proven in an erbium complex with an extremely long ligand of diphosphine dioxide type.[5] This demonstrates that the fine control over the length and flexibility of the ligand, as well as the electron donating/withdrawing abilities of the substituents on its backbone, are of crucial importance.

Compared with the solid-state structures of uncoordinated $dpppO_2$ and $dppeO_2$,[6] the conformations of both ligands in **1** and **2** are preserved. The P=O bonds of $dppeO_2$ in **2** are approximately antiparallel to each other (an *anti* conformation), while the P=O bonds of $dpppO_2$ in **1** lie almost in the plane of the pyridine ring with a *syn* conformation. Also, the double-bond character of the P=O bonds in free ligands is quite unaffected upon coordination. Average Pr−O bonds to nitrate groups are about 0.2 Å longer than the Pr−O distances pointing toward phosphorus. Corresponding values and other important bond lengths and angles are listed in Table 1, and the coordination polyhedra of both compounds are depicted in Figure 1.

Both structures can be considered as consisting of the $Pr(NO_3)_3$ centers, accepting either four (**1**) or three (**2**) additional neutral ligands. In **1**, this leads to tetrameric, almost square units, where every $dpppO_2$ bridge forms one side of such a tile. Due to the T-shaped coordination in **2**, the building blocks are approximately rectangular with one ligand at the shorter side, and two ligands at the longer sides of the tile (Figure 2). In terms of previously used classification, the tiling pattern in **2** can be labeled as herringbone or “parquet floor” architecture.[7] With respect to the number of spacer ligands in the tile and their number in the Pr(III) coordination sphere, these 2D networks are of 4^4 (**1**) and 6^3 (**2**) type. The average Pr−Pr separations are ca. 11.2 and 9.5 Å, resulting in the tile diagonal dimensions of ca. 15.2 × 16.4 Å^2 and 16.3 × 23.4 Å^2 in **1** and **2**, respectively. The

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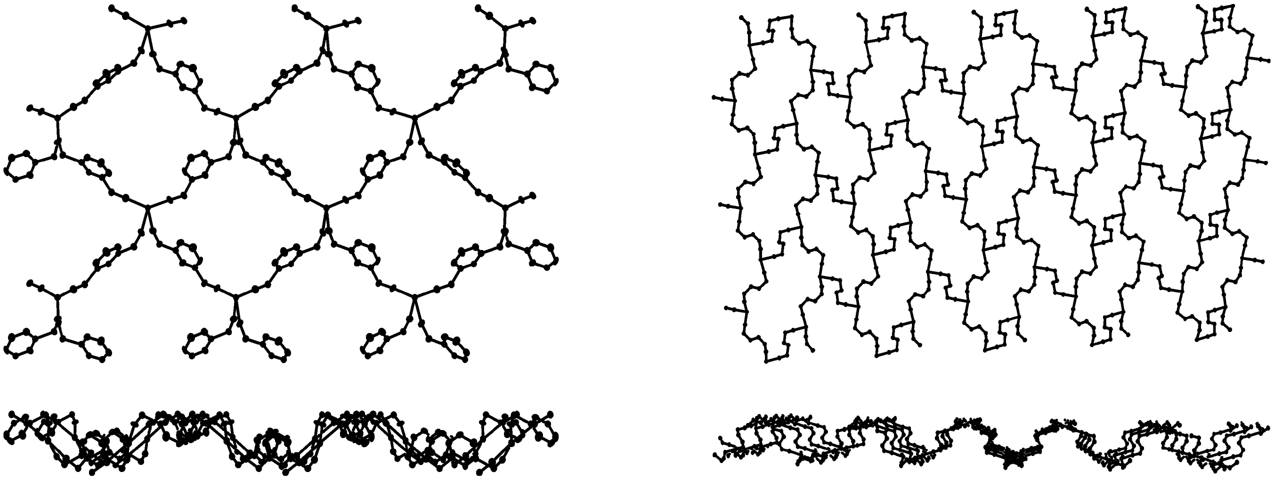

Figure 2. Top and lateral views on 2D polymeric layer in **1** (left) and **2** (right). All hydrogen atoms, phenyl groups, and nitrate ligands were omitted for clarity. Praseodymium atoms are at the four- and three-connected centers, respectively.

cavities inside the tiles are necessarily hydrophobic in nature, being strewn with phenyl groups. Viewed laterally, the single undulating layers propagate in the crystallographic *ab* plane in **1**. In **2**, the positioning of polymeric layers within the unit cell can be most appropriately described as interleaving the crystallographic $(10\bar{1})$ planes. The atoms are vertically aligned in successive layers, and the stacking of cavities thus gives rise to channels running perpendicularly to the 2D coordination networks. The distances between the praseodymium atoms in adjacent layers in **1** and **2** are 12.8 and 13.0 Å, respectively. The interplanar space in **1** is disorderly occupied by dichloromethane molecules, in approximate 2:1 overall stoichiometry (two CH_2Cl_2 molecules per monomeric $Pr(NO_3)_3(dpppO_2)_2$ unit).

An extensive system of covalent bonds results in the insolubility of the complexes in common solvents, and also significantly affects their thermal behavior, as documented by TGA. While only **1** melts at 285 °C, both coordination polymers decompose in two relatively sharp steps. The first is a highly exothermic reaction corresponding to organic mass combustion and occurs at 360 (**1**) and 373 °C (**2**). The second event is slightly broader and endothermic. Above 600 °C, the samples consist of a mixture of praseodymium phosphates (confirmed by X-ray powder diffraction).

In conclusion, we have shown that the neutral ligands of diphosphine dioxide type with larger bite angles are capable of forming two-dimensional coordination networks. The ligands of the $R_2P(O)-X-P(O)R_2$ general formula can be relatively easily modified in their central moiety X, leading to increased/decreased flexibility on one hand, and to longer/shorter backbones with the corresponding bite angles on the other. We believe these ligands offer an attractive possibility for the control of the separation of metal centers (nodes) by tuning the length of the P−X−P ligand (spacer) and thus will provide a valuable tool to crystal engineers not only in lanthanide coordination chemistry, but in supramolecular design as a whole.[8]

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Supporting Information Available: Crystallographic data of **1** and **2** and a separate PDF file with the detailed description of experimental preparations. This material is available free of charge via the Internet at http://pubs.acs.org.

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