Synthesis and Characterization of the One Dimensional Coordination Network of $[Pr(bpydo)_4(H_2O)_3](ClO_4)_3 \cdot bpydo \cdot 5.5H_2O$



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I hereby recognize and pledge to fulfill my responsibilities as defined in the Honor Code, and to maintain the integrity of both myself and the College community as a whole.

Pledge:_____

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Abstract

Coordination chemistry is based on the interactions between the Lewis acid and the Lewis base. Lanthanide perchlorates (Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, and Yb), when combined with 4,4'-bipyridine-*N,N'*-dioxide,bpydo, in aqueous solution, were found through X-ray crystallography to form three distinct coordination complexes based on location in the series. The first structure, which occurs for Pr, Nd, Sm, Eu, Gd, and Tb, was analyzed in depth for Pr^{3+} and determined to have the equation $[Ln(bpydo)_4(H_2O)_3](ClO_4)_3 \cdot bpydo \cdot 5.5H_2O$. It is a 1D chain with space group $P2_1/c$ with a=16.9, b=21, c=17.4.

Introduction

In recent years, lanthanide coordination network research has gained popularity in the field of coordination chemistry. Most previous coordination networks have been created using transition metals as Lewis acids. The transition metals contain *d*-orbitals that allow for coordination to ligands, which act as the Lewis bases. However, transition metals have smaller atomic and ionic radii than lanthanides (at times half as large), which limits the size and the number of ligands that can be coordinated to the metal ion.[1] Lanthanides offer the possibility of greater connectivity at the metal center. While lanthanide coordination network chemistry is still relatively new, there is vast potential for the application of the networks. The pores that can potentially be created by coordination networks could be used to selectively bind molecules and catalyze reactions.[2] These pores could also be used for adsorption and ion exchange processes. The networks would attract molecules into the pores and encapsulate them due to their structural rigidity and specificity.[3]

Supramolecular Chemistry and Self-Assembly

Supramolecular chemistry has come to have multiple meanings. It can focus on the intermolecular chemistry aspect of self-assembly, which defines the interactions between different species. It has also come to be interpreted as intramolecular coordinate covalent bonds between metals and ligands. The different types of interactions are shown in Table 1.

Intramolecular Forces	Intermolecular Forces
Covalent Coordinate Covalent/ Dative Bonding	London Dispersion Forces π-π Stacking Cation-π Attraction Dipole-Dipole Forces Ion-Ion Electrostatic Forces Ion-Dipole Interactions Hydrogen Bonding

Table 1

Intramolecular interactions, such as covalent and coordinate covalent, are often short-range and strong. Intermolecular interactions, in contrast, are generally longer-range and therefore weaker.[4] However, many intermolecular interactions working together can be quite strong in the aggregate. Supramolecular chemistry typically consists of coordinate covalent bonding and intermolecular bonding.

The self-assembly process involves the use of engineered subunits that have specific attractions to each other. This is based on interactions between functional groups, for example the attraction of charge or shape confirmation. Shape is a factor because there may only be a specific amount of space for this to occur in. These interactions occur without intervention by the chemist. This is possible because each molecule has specific "codes" based on its structure that determine the types of interactions it is able to make, such as dipole-dipole interactions, hydrogen bonds, dative bonds, or hydrophobic interactions.[5]

Coordination Chemistry

In coordination networks, the ligands and metals interact through dative bonding that can be understood using Lewis Acid/Base theory.[5] The bonding creates distinct one, two, or three dimensional networks. These coordination networks can then further interact through hydrogen bonding or π-π stacking.[6]

The formation of coordination networks is explained through the theory of Lewis acids and bases. Lewis acids are electron pair acceptors and Lewis bases are electron pair donors. The metals of choice act as Lewis acids since they can accept electrons due to their positive charge that creates space for the electrons to situate. Lewis bases can donate their lone electron pairs to the metals to create coordination networks.[7] These networks can interact to form different layers. A one-dimensional layer is made up of simple chains that are usually linear or zigzag. [8] Two-dimensional systems occur for square planar or octahedral geometries; and three-dimensional systems occur for tetrahedral and some octahedral metals.[2, 9] 4, 4'-bipyridine-*N,N'*-dioxide (bpydo) has been used with transition metals in order to form both 1D chains and 2D sheets. The 1D chains are due to the metal node only allowing for two connections. The ligand, bpydo, is acting as a bridge to connect the metal centers and can connect in either syn or anti conformations. In one example, Cu^{2+} is being bonded to four bpydo ligands, two of which bridge to the neighboring copper metal center, while the other two are terminal. This continues in a linear fashion, creating a long chain (Fig. 1).[10]

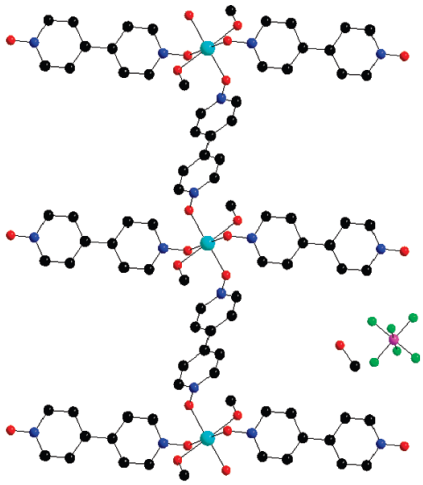


Fig. 1: 1D chain of Cu^{2+} and bpydo with PF_6^{1-} and CO in the pores of $[Cu(bpydo)_2(OHMe)_2(\mu\text{-}L)]\cdot 2PF_6\cdot n(solv)$ in ball and stick form where Cu=auqa, C=black, N=blue, O=red, F=green and P=pink.[10]

Copper (II) can also create 2D networks. In one case, the copper center is coordinated to six bpydo ligands in a distorted octahedral fashion. The ligands, all of which are bridging, create π-π stacking interactions in the aromatic ring and stack to form eclipsed 2D sheets (Fig. 2).[10]

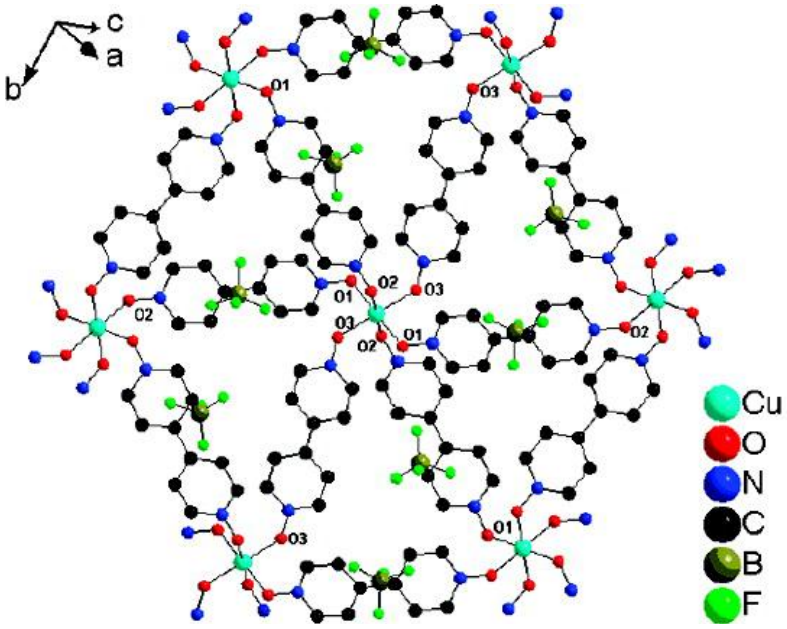


Fig. 2: Cu^{2+} connected to six bpydo with BF_4^{1-} in the pores $[Cu(\mu\text{-}bpydo)_3]\cdot 2BF_4$.[10]

Three dimensional structures can also be created. These occur less often because the metal center must be large enough to be able to accommodate multiple bridging ligands. Cheng et al. used lanthanide-transition metal combinations to form a 3D network with the ligands 1, 2-benzenedicarboxylic acid (H_2bdc) and isonicotinic acid (Hina) (Fig. 3).[11]



Fig. 3: 1,2-benzenedicarboxylic acid and isonicotinic acid.

Ce^{3+} and Cu^{+} are combined to create an intertwining framework. One Ce^{3+} center is a tricapped trigonal prism and is bonded to two waters, five ina ligands, and two bdc ligands. The second Ce^{3+} in the unit cell is a bicapped trigonal prism bonded to one water, five ina ligands, and two bdc ligands. The third Ce^{3+} metal center is also a bicapped trigonal prism and is bonded to one water, six ina ligands, and one bdc ligand. The Cu^{+} is able to bridge and create the 3D motif (Fig. 4).[11]

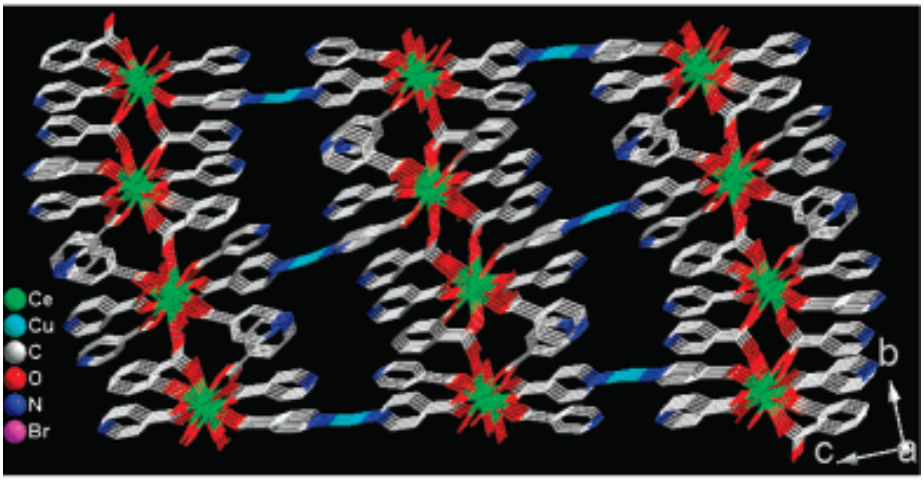
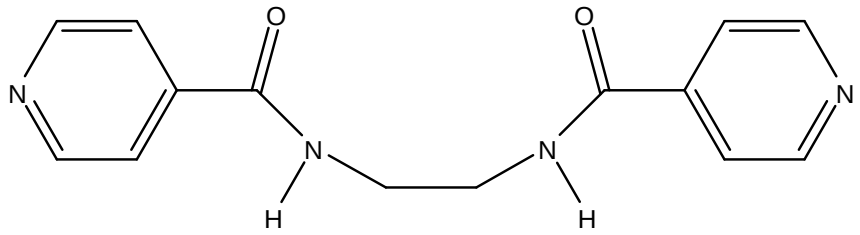


Fig. 4: Ce^{3+} metal atoms connected to 1, 2-benzenedicarboxyl and isonicotine with interconnecting Cu^{+} atoms in wire frame of $[Ce_3(ina)_8(bdc)(H_2O)_4][Cu_7Br_6]$.[11]

Coordination Networks with Transition Metals

Early in the synthesis of coordination networks, the focus was on transition metal cations. These metals generally allow six or fewer attached groups due to their atomic size. Some common transition metals used are copper, cadmium, iron, and manganese.[10] Copper (II), specifically, has been used and found to coordinate in an octahedral geometry to six groups, four equatorial ligands [bis(pyridinecarboxamido)alkane] and two axial waters in a 2D structure (Fig. 5).



bis(pyridinecarboxamido)alkane

Fig. 5: [bis(pyridinecarboxamido)alkane] ligand with two CH_2 molecules in the backbone

The layers are created by coordinate covalent bonds that create pockets for hexafluorophosphate inclusion. The network is depicted as a wire frame. The layers are held together by hydrogen bonding that occurs between the axial waters that are coordinated to the metal center, shown in red, and the oxygen atoms from the ligands. The PF_6^{1-} molecules, in green, are space filled. These anions sit in the space between to two layers, which are offset (Fig. 6).[12]

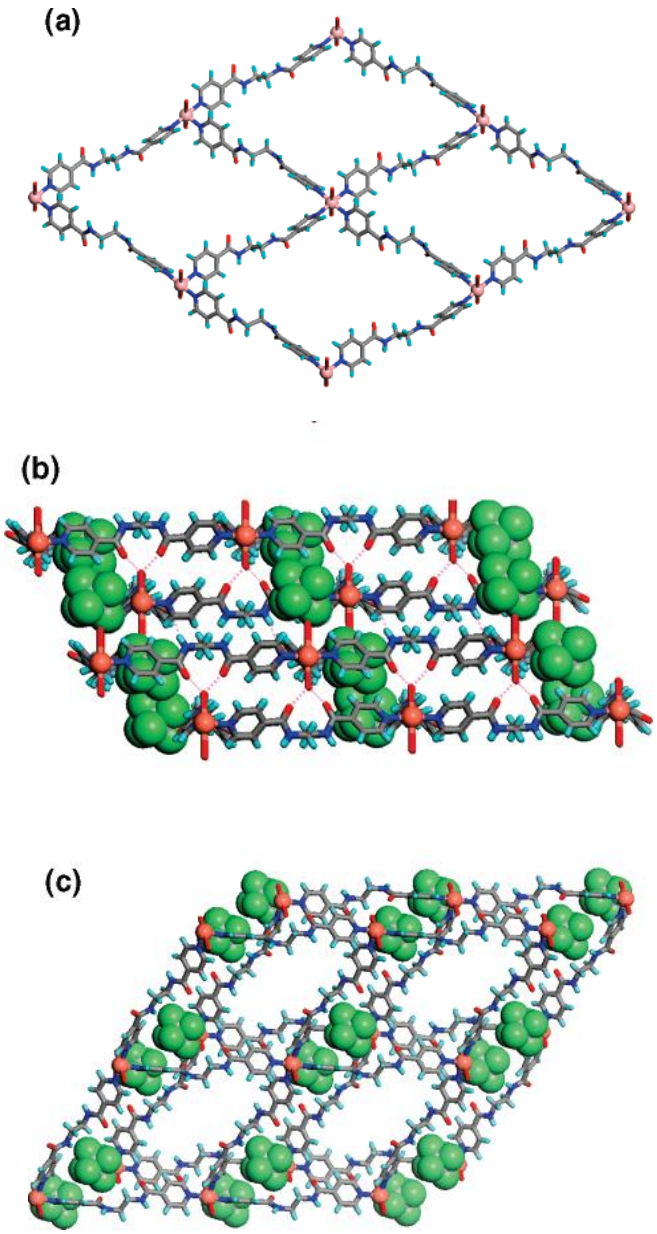


Fig. 6: Structures of Copper being coordinated to bis(pyridinecarboxamido)alkane(L) $[Cu(L)_2(H_2O)_2](PF_6)_2(H_2O)_2$ in wire frame form. (a) 2-D layer of the structure showing the cavities; (b) side-view of the structure showing the hydrogen bonds between layers (c) top view showing the pores available for PF_6^{1-}, which is space filled. Cu=orange, C=gray, H=aqua, N=blue, O=red, and F=green.[12]

In general, the number of ligands coordinated to a metal cation is restricted by the cation size. Since the transition metals are slightly smaller in radius than lanthanides, the

transition metals cannot be coordinated to large numbers of bulky ligands. It is hoped that these limitations will be overcome with the use of lanthanide metal cations.

N-aromatic Ligands

Nitrogen ligands have been widely used because of their basic lone electron pairs and widespread commercial availability. They are able to coordinate to a variety of metal centers through dative bonding. Aromatic functional groups are important in the structural layering of a crystal. They are able to participate in π-π stacking to order the networks in different arrays by influencing the interactions based on their electron density.[13] Commonly used ligands are pyrazine and Bipyridine (Fig. 7).

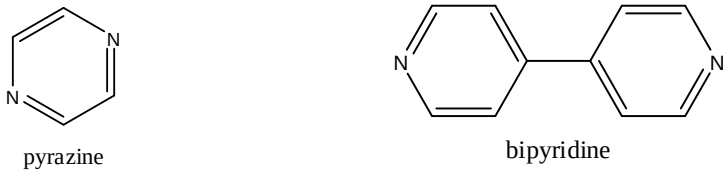
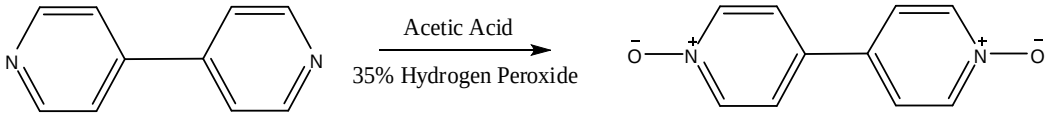


Fig 7: Structures of common ligands pyrazine and bipyridine.

N, N'-Dioxide Ligands

It has been determined by Heitzman and coworkers that since, N-aromatics are borderline Lewis bases, they need to be modified for increased specificity and stability with the lanthanides. In the case of hard acids, i.e. the lanthanides, the base ligand needs to be hard in order to have a stronger, more complementary bond.[14] One such way is to convert the N-aromatic to an N-oxide (Scheme 1).[15]



Scheme 1: Parent ligand reacted to create N,N'-dioxide ligands.[15]

Harder acids that are highly charged will form slightly more ionic bonds, which is why a hard base like oxygen is able to bond better than nitrogen. Oxygen also makes the ligand longer, which decreases the steric hindrance with the metal and increases the flexibility of the complex; this is important when the radius is large, as is the case for the lanthanides, and when one is trying to achieve high coordination numbers.[16-18]

Lanthanides

Lanthanide chemistry involving coordination networks has become an interesting area of research because of the potential to form new coordination environments and networks. The lanthanide series most often form +3 cations through the loss of the *s* and *d* electrons in the valence shells. The remaining *f* valence electrons have poor shielding effects, causing the valence electrons to be drawn closer to the nucleus. The lanthanide contraction causes the lanthanides to decrease in size across the period, but these metals are still substantially larger than the transition metals.

The lanthanide contraction makes the lanthanide cations more resistant to polarization than transition metals, and thus the lanthanides are characterized as hard acids. In order to be a hard acid, size and charge must be considered. Even though lanthanides are larger in comparison to the other metals in the periodic table, the +3 charge is able to overcome the ionic radius to make them hard. Hard acids form strong bonds with hard bases to give complexes in which the bonds have a significant ionic character.[19] Hard bases are typically small, electronegative centers that are weakly polarizable. A characteristic hard base is oxygen, because its bonding will have substantial ionic character and oxygen has a high electronegativity.

In the formation of lanthanide coordination networks, N-oxide donor ligands should be utilized due to the potential compatibility of the hard acids and bases. The oxygen will form a dative bond, of substantial ionic character, with the lanthanide and donate two, or more, of its electrons (Fig. 8).

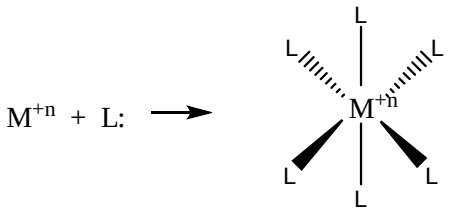


Fig. 8: Lewis Acid/ Base formation of dative bond. (M= metal, L=ligand).

The size of the lanthanide cations and the fact that bonding is more ionic and less directional allows larger numbers of ligands to be coordinated, which has led to the formation of new networks with previously unseen topologies. [12-15] Using samarium and erbium, coordination networks with ten and nine coordinate metal cations, respectively, were made using the ligand 4,4'-bipyridine-*N,N'*-dioxide (bpydo). For Sm^{3+}, the oxygen atoms from each bonding bpydo ligand and nitrate form a hexadecahedron environment around the central atom. The oxygens around Er^{3+} form a distorted tricapped trigonal prism (Fig. 9).[13]

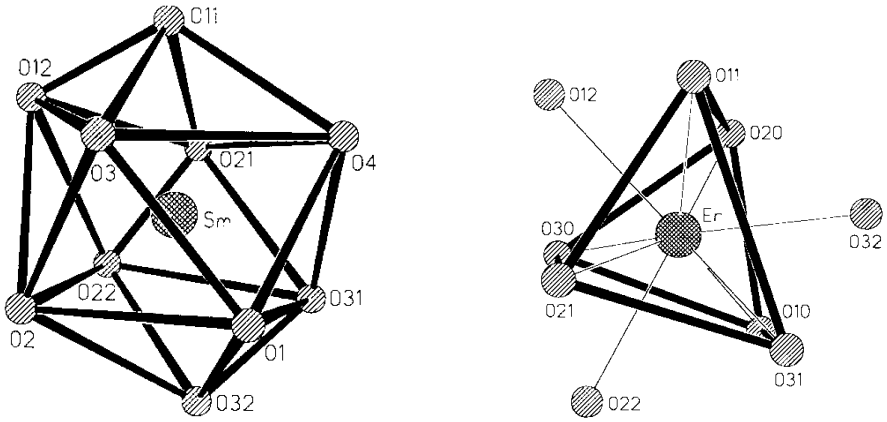


Fig. 9: Coordination environments of Sm^{3+}, left $[Sm(bpydo)_2(NO_3)_3]\cdot 0.5H_2O$, and Er^{3+}, right $[Er_2(bpydo)_3(NO_3)_6]\cdot CH_3OH$, with the coordinated oxygens.[13]

Many of the lanthanides have been used with pyrazine-dioxide, pzdo. In the case of the research by Sun, et al, each of the lanthanides tested (La, Ce, Sm, Eu, Gd, Tb, Y, and Pr) were found to be isomorphous and connected to eight pzdo ligands in an octahedral geometry (Fig. 10).

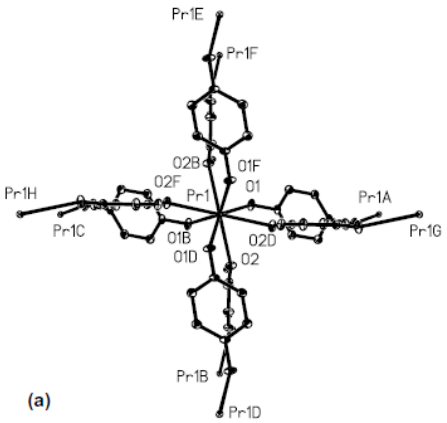
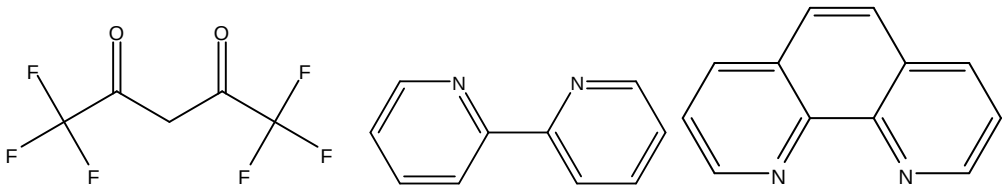


Fig. 10: Pr^{3+} as the metal center connected to eight pzdo ligands. Other metals were La, Ce, Sm, Eu, Gd, Tb, and Y of the formula $[Ln(pzdo)_4](ClO_4)_3$.[20]

Others have found, however, that there are changes in the structure of complexes across the lanthanide series. It has been suggested that the change of conformation is due to the ion size.[21] The metals that occur later in the series are slightly smaller than those that occur at the beginning. The larger radii are able to accommodate more coordinating molecules. When using 1, 1, 1, 5, 5, 5-hexafluroro-2, 4-pentanedione (hfpd) and either 2,2'-bipyridine (bpy) or 1,10-phenanthroline (phen) with Er, Tb, Ho, Yb, La, Sm, Ce, Pr, and Nd, all in the 3+ stage, different structures were determined based on the ionic radii (Fig 11).



1,1,1,5,5,5-Hexafluoro-2,4-pentanedione 2,2'-bipyridine 1,10-phenanthroline

Fig 11: Ligands hfpd, bpy, and phen.

The earlier elements, La, Sm, Ce, Pr, and Nd were ten coordinated in one of two complexes: $[Ln(hfpd)_3(bpy)_2]$ for La and Sm and $[Ln(hfpd)_3(phen)_2]$ for La, Ce, Pr, and Nd (Fig. 12).[21]

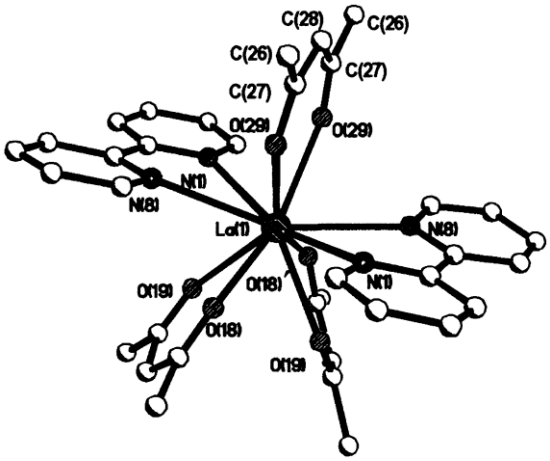


Fig. 12: La(III) center coordinated to two bpy and three hfpd, $[La(hfpd)_3(bpy)_2]$. The same structure occurs for Sm. Similar structures are observed for La, Ce, Pr, and Nd except the bpy is replaced by phen.[21]

The later lanthanides tested were found to be eight-coordinated to three hfpd ligands and either one bpy or one phen ligand (Fig. 13).

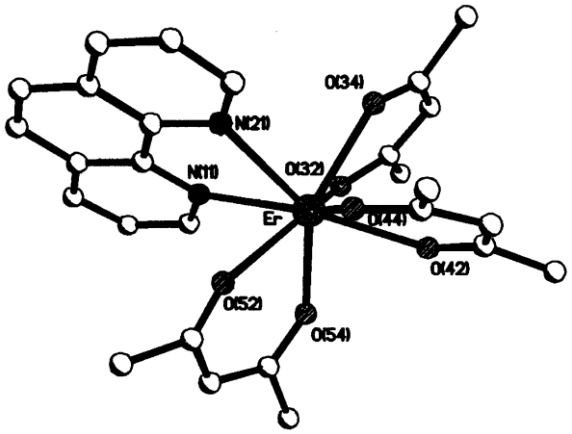


Fig. 13: Er(III) center coordinated to one phen ligand and three hfpd ligands, $[Er(hfpd)_3(phen)]$. The same structure occurs for Tb, Ho, and Yb while Dy, Ho, and Yb are similar except coordinated to bpy.[21]

Reason for Research

Research on lanthanide coordination networks has shown much promise. My previous work created crystals of lanthanides coordinated to the 4, 4'-bipyridine-*N*-*N'*-dioxide ligand (bpydo). In preliminary studies, it was noticed that there were three types of networks created from the same reaction conditions, depending on the lanthanide used. The first type of network is coordinated to five ligands and three waters. When the structure is grown and layered, it forms a zigzag pattern. The second crystal structure formed has three unique metal centers, two of the metal centers bind to four ligands and four waters, and one binds to two ligands and three waters that are disordered. What is interesting about the structure is that, when layered, it forms a basket weave pattern (Fig. 14).

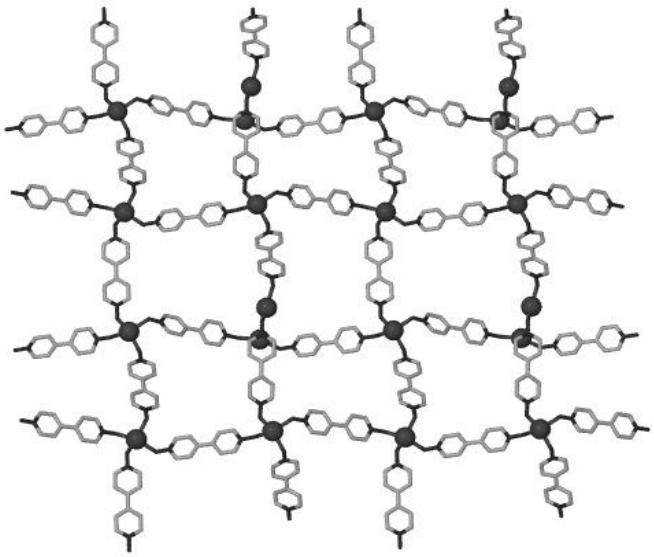


Fig 14 : 2D Basket weave pattern.[22]

The third structure was a hydrated complex with the bpydo ligands noncoordinated.[22]

It has been proposed in other research that different arrangements can be due to the stability and reaction time allowed for the networks to form.[23] It could also potentially

be due to solvent changes as the crystals are growing in solution. A third plausible cause could be due to ionic radius size as was presented earlier. The purpose of the proposed research is to determine and understand how the multiple products are formed in the reaction. In order to examine the structural formation, solvent amounts will be altered along with the ratios of solvent, ligand, and lanthanide.

Experimental

Synthesis of 4, 4'-bipyridine-*N, N'*-dioxide·$2H_2O$[24]

All chemicals were from Aldrich Chemicals. 4, 4'-bipyridine-*N, N'*-dioxide was synthesized by combining 98 % 4, 4'-bipyridine (0.0640 mol) with glacial acetic acid (1.305 mol) and 30 % hydrogen peroxide (0.130 mol) for three (3) hours in a hot oil bath kept at a constant temperature between 70-80 ºC. Additional hydrogen peroxide (0.0900 mol) was added and mixing was continued for nineteen (19) hours under the same conditions. Acetone (1 L) was added and the product was collected by vacuum distillation until the acetone had evaporated. The crystals were recrystallized in water and excess acetone. The 4, 4'-bipyridine-*N, N'*-dioxide (11.6513 g) was then collected by vacuum filtration.

Synthesis of Lanthanide Coordination Networks with 4, 4'-bipyridine-*N, N'*-dioxide

$Dy(ClO_4)_3$ (40 wt%), $Er(ClO_4)_3$ (40 wt%), $Eu(ClO_4)_3$ (50 wt%), $Ho(ClO_4)_3$ (40 wt %), and $Pr(ClO_4)_3$ (40 wt%) were from Aldrich Chemicals as aqueous solutions. $Gd(ClO_4)_3$ (50 wt%), $Nd(ClO_4)_3$ (50 wt%), $Sm(ClO_4)_3$ (50 wt%), $Tb(ClO_4)_3$ (50 wt%), and $Yb(ClO_4)_3$ (50 wt%) were from Sigma Chemicals as aqueous solutions.

Trail 1 [22]

4, 4'-bipyridine-N, N'-dioxide·$2H_2O$ (1 mmol) and $Ln(ClO_4)_3$ (Ln=Dy, Er, Eu, Gd, Ho, Nd, Pr, Sm, Tb, and Yb; 0.25 mmol) were combined in H_2O (9 mL) and placed in a hot water bath to dissolve and were then allowed to sit. Clear, colored crystals were collected for each within several months.

Trial 2

4, 4'-bipyridine-N, N'-dioxide·$2H_2O$ (1 mmol) and $Ln(ClO_4)_3$ (Ln=Dy, Er, Eu, Gd, Ho, Nd, Pr, Sm, Tb, and Yb; 0.25 mmol) were combined in H_2O (6 mL) and placed in a hot water bath to dissolve and were then allowed to sit. Clear, colored crystals formed for Dy, Eu, Ho, Nd, Pr, Sm, and Tb within a month.

Trial 3

4, 4'-bipyridine-N, N'-dioxide·$2H_2O$ (1 mmol) and $Ln(ClO_4)_3$ (Ln=Dy, Er, Eu, Gd, Ho, Nd, Pr, Sm, Tb, and Yb; 0.25 mmol) were combined in H_2O (12 mL) and placed in a hot water bath to dissolve and were then allowed to sit. No crystals have yet been detected.

Trial 4

4, 4'-bipyridine-N, N'-dioxide·$2H_2O$ (0.5 mmol) and $Ln(ClO_4)_3$ (Ln=Dy, Er, Eu, Gd, Ho, Nd, Pr, Sm, Tb, and Yb; 0.125 mmol) were combined in H_2O (2.25 mL) and placed in a hot water bath to dissolve and were then allowed to sit. Clear, colored crystals formed each within 12 hours.

Crystal Data

The Bruker AXS SMART APEX CCD diffractometer was used for x-ray crystallography. The structure was solved and refined using the programs SHELXS-97 (Sheldrick, 1990) and SHELXL-97 (Sheldrick, 1997) respectively. The program X-Seed (Barbour, 1999) was used as an interface to the SHELX programs, and to prepare the figures. Crystallographic details, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen bonds are listed in tables 1-6 in the Appendix.

Two of the anions are disordered over two non-symmetry related positions. The perchlorate anion consisting of atoms Cl2 and O18-O20 refined to a site occupancy of 0.52529, and the perchlorate anion consisting of atoms Cl2B and O18B-O20B refined to a site occupancy of 0.47471. The perchlorate anion consisting of atoms Cl3 and O22-O25 refined to a site occupancy of 0.63974, and the perchlorate anion consisting of atoms Cl3B and O22B-O25B refined to a site occupancy of 0.36026.

For both positions of these disordered anions, atoms were refined with geometric and thermal restraints using the SADI, SIMU, DELU restraints in SHELXL. Atoms Cl3B and O22B-O25B were refined with isotropic thermal parameters. Three of the non-coordinating water molecules were also disordered over two non-symmetry related positions. Atom O2W refined to a site occupancy of 0.49474, and atom O2WB refined to a site occupancy of 0.50526. Atom O3W refined to a site occupancy of 0.44738, and atom O3WB refined to a site occupancy of 0.55262. Atom O7W refined to a site occupancy of 0.62744, and atom O7WB refined to a site occupancy of 0.37256. Site occupancy refinement of atoms O4W and O5W indicated partial occupancies of

approximately 0.5; therefore the occupancies of these atoms were set to 0.5. ISOR restraints were applied to O22, O23,O24, O25, O21B O4W, O5W, O6W, O7W, O7WB, O3WB.

All other non-hydrogen atoms were refined with anisotropic thermal parameters. All non-water hydrogen atoms were included in calculated positions and refined as riding models with fixed *Uiso*=1.2 *Uiso* of the carbon atoms to which they are bonded. Hydrogen atoms were located for the coordinated water molecules and one of the non-coordinated water molecules (O1W). The hydrogen atoms of thes water molecules refined with bond distanced restrains of 0.85Å using the DFIX command in SHELXL. The hydrogen atoms of other non-coordinated water molecules (O2W, O2WB, O3W, O3WB, O4W, O5W, O6W O7W, and O7WB) could not be located.

Elemental Analysis

Elemental analysis was performed on all of the samples from Trial 4 using the *Perkin Elmer 1400 Series II C H N S/O Analyzer*. Only Nd, Gd, and Eu are presented since these are all Compound **1** structures.

Table 2: Found values from elemental analysis

	C	H	N	
Nd	39.48	3.23	10.1	
	39.77	3.54	9.96	
	39.63	3.47	9.69	
	39.62667	3.413333	9.916667	Average
Gd	39.55	3.53	9.31	
	39.34	3.51	9.12	
	39.29	3.56	9.3	
	39.39333	3.533333	9.243333	Average
Eu	39.41	3.42	9.13	
	39.4	3.38	9.29	
	39.42	3.52	9.14	
	39.41	3.44	9.186667	Average

Table 3: Analyzed for and average found values from elemental analysis

Element		C	H	N
Eu	Analyzed for	38.88354	3.720163	9.07174
	Found	39.41	3.44	9.186667
Gd	Analyzed for	38.75088	3.707473	9.040796
	Found	39.39333	3.533333	9.243333
Nd	Analyzed for	39.07896	3.738863	9.11734
	Found	39.62667	3.413333	9.916667

Results and Discussion

Using the 4, 4'-bipyridine-*N,N'*-dioxide, bpydo, and Lanthanide perchlorates, three different structures were formed. Table 4 shows the different unit cells for each of the crystals analyzed by x-ray crystallography from trial 1 and trial 4.

Table 4: Unit cell parameters for Ln(III) tested.

reaction	a	b	c	α	β	γ	Metal	
Trial 1	16.9538	21.2921	17.4278	90	109.7198	90	Pr	1D ZIGZAG
Trial 4	16.9538	21.2921	17.4278	90	109.7198	90	Pr	
Trial 1	16.9587	21.2370	17.4413	90	109.6892	90	Nd	
Trial 4	17.9587	21.2370	18.4413	90	109.6892	90	Nd	
Trial 4	16.9455	21.1279	17.4586	90	109.544	90	Sm	
Trial 4	16.9378	21.0881	17.4581	90	109.4935	90	Eu	
Trial 1	16.9244	21.0604	17.4624	90	109.493	90	Gd	
Trial 4	16.9244	21.0604	17.4624	90	109.493	90	Gd	
Trial 1	16.9929	21.2257	17.4535	90	109.6968	90	Tb	
Trial 4	26.1437	26.1437	21.4604	90	90	90	Tb	2D BASKET
Trial 4	26.1107	26.1107	21.4339	90	90	90	Dy	WEAVE
Trial 1	26.1269	26.1269	21.4523	90	90	90	Dy	
Trial 1	26.1173	26.1173	21.4674	90	90	90	Ho	
Trial 4	26.016	26.016	21.39	90	90	90	Ho	
Trial 1	26.0834	26.0834	21.4185	90	90	90	Er	
Trial 4	26.0834	26.0834	21.4185	90	90	90	Er	
Trial 1	26.0654	26.0654	21.4424	90	90	90	Yb	
Trial 1	17.0297	17.3969	17.4336	60.876	82.095 7	79.477	Er	0D HYDRATED
Trial 4	17.0109	17.3666	17.4187	60.915	81.967	79.417	Yb	COMPLEX

The 1D zigzag structure for Pr^{3+}, compound 1, was the focus of analysis. The structures were the same from the original synthesis and from the 0.5 mmol bpydo and 0.125 mmol Ln(III)ClO_4. The Lanthanide centers were coordinated to five bpydo ligands and three waters (Fig. 15). Of the ligands, two of them are bridging to other metal centers while the other three are terminal. The formula for this compound is $[Ln(bpydo)_4(H_2O)_3](ClO_4)_3 \cdot bpydo \cdot 5.5H_2O$.

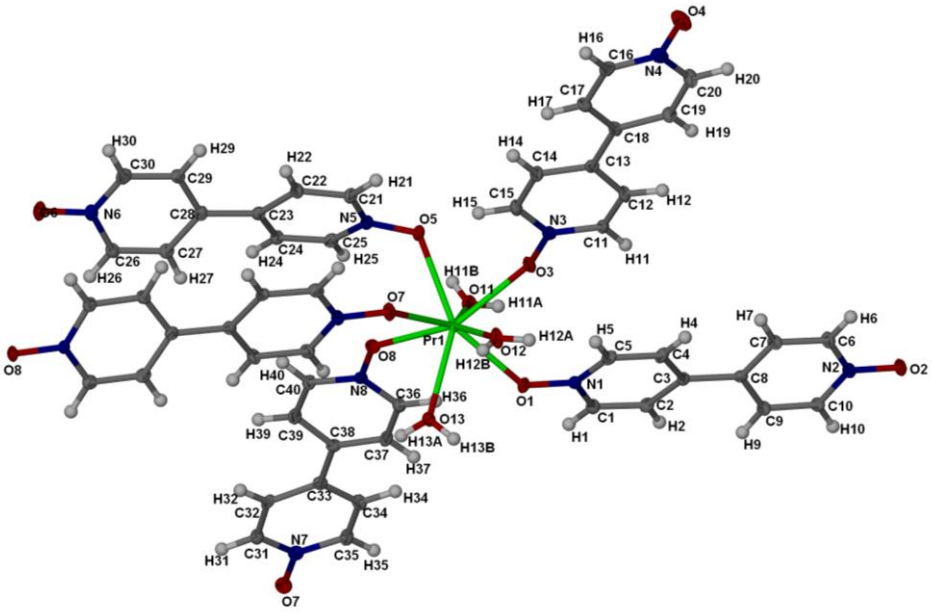


Fig.15: Ball and stick coordination environment for Ln^{3+} cation in $[Ln(bpydo)_4(H_2O)_3](ClO_4)_3 \cdot bpydo \cdot 5.5H_2O$ where Ln=Pr, Nd, Sm, Eu, Gd, and Tb. Pr=green, O=red, N=blue, gray, and H=white, unless specified elsewhere.

The distance between the Pr^{3+} center and oxygen atoms was approximately 2.4 Å. The ligands and waters coordinate to the metal in a distorted square anti-prismatic fashion: there are two square antiprisms and eight triangular prisms. The two squares are rotated over each other so that the corners of one lie over the center of the other squares connecting line. The angles of two adjacent oxygen atoms with the Pr^{3+} as the vertex range from 70 to 81 degrees (Fig. 16).

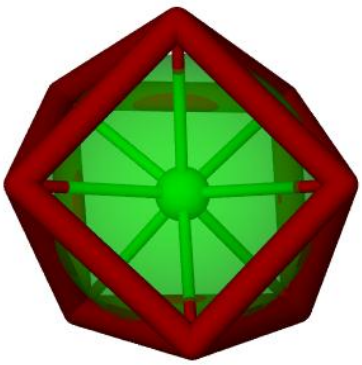


Fig. 16: Space filled Pr^{3+} metal center showing the distorted square anti-prismatic coordination environment.

The ligands that are bridging, oxygens 7 and 8, create a zigzag 1D chain between the metal centers. The metal centers are approximately 6.3 Å apart (Fig. 17).

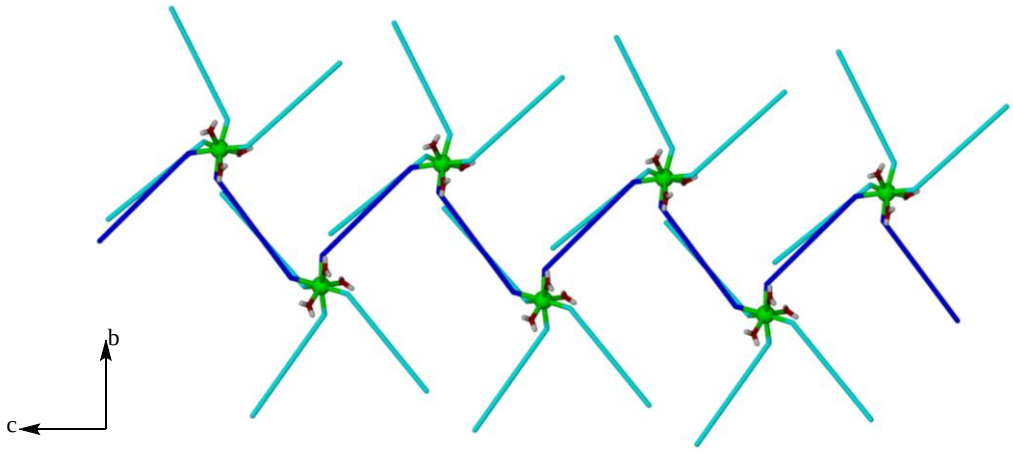


Fig.17: Schematic representation of the 1D chain seen in $[Pr(bpydo)_4(H_2O)_3](ClO_4)_3 \cdot bpydo \cdot 5.5H_2O$. Bridging ligands are represented by blue rods while terminal ligands are represented by aqua rods.

The chains are also involved in hydrogen bonding between noncoordinated ligands and terminal ligands with the coordinated waters. Each of the waters coordinated to the Pr^{3+} metal center has one or both hydrogens involved in a hydrogen-bond with a bpydo ligand. All of the terminal ligands are hydrogen bonded to either a water on a neighboring metal center or a noncoordinated water, and each non-coordinated ligand is hydrogen bonded to two metals (Fig. 18).

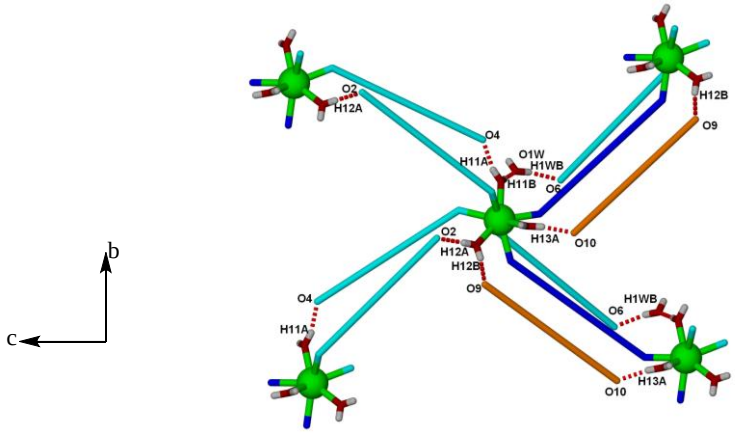


Fig. 18: Hydrogen bonds between the waters and bpydo ligands. Terminal ligands are aqua, bridging ligands are blue, and non-coordinated ligands are orange rods.

Table 5 gives the distances between each of the hydrogen bonds from Figure 18. The first column describes the entire interaction being measured between the donor oxygen, D, and the acceptor oxygen, A. The second column is the distance of the covalent bond between the donor oxygen and the hydrogen. The third column is the distance of the actual hydrogen bond. The fourth column gives the distance between the donor oxygen and the acceptor oxygen. The last column gives the angle that occurs for the entire bonding complex.

Table 5: Hydrogen bond distances for Compound **1** in degrees and Å.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(12)-H(12A)...O(2)#4	0.833(18)	1.809(19)	2.641(4)	177(4)
O(12)-H(12B)...O(9)	0.845(19)	1.87(2)	2.696(3)	167(5)
O(11)-H(11A)...O(4)#5	0.827(18)	1.83(2)	2.632(4)	163(3)
O(11)-H(11B)...O(1W)#6	0.832(18)	1.84(2)	2.658(4)	170(4)
O(13)-H(13B)...O(9)#7	0.85(2)	1.90(2)	2.737(4)	166(5)
O(13)-H(13A)...O(10)#1	0.835(19)	1.87(2)	2.693(4)	170(5)
O(1W)-H(1WA)...O(5)#8	0.828(19)	2.21(2)	3.027(4)	168(4)
O(1W)-H(1WB)...O(6)#2	0.831(19)	1.94(3)	2.738(4)	161(5)

The ligands are also involved in π-π stacking interactions (Fig. 19). The middle ligand in the stacking complex is covered above and below by other bpydo ligands, either from noncoordinated ligands or from neighboring chains. Oxygens 2, 4, 6, 7, and 8 are coordinated to the central metal atom. The terminal ligands are 2, 4, and 6. Each of these oxygens hydrogen bonds with a neighboring metal atom. Oxygens 7 and 8 are on either end of the bpydo ligand that bridges the Pr^{3+} metal centers to form the chains. Oxygen 10 is part of a noncoordinated ligand that occurs in the pores. Oxygens 1, 3, and 5 are coordinated to neighboring metal centers, which are depicted, and each of these ligands interacts with the central metal through hydrogen bonds.

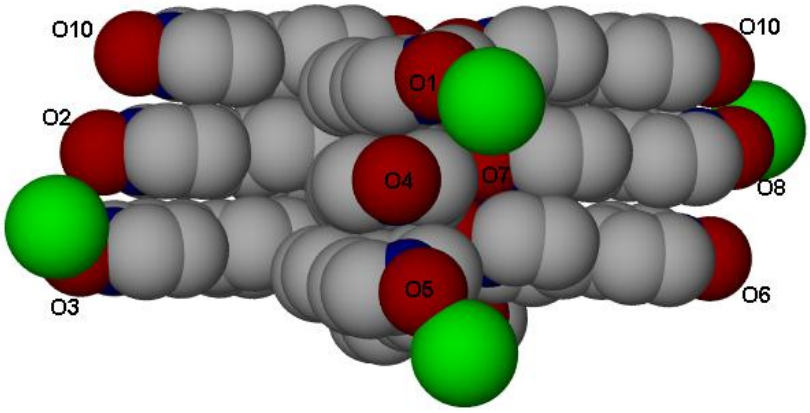


Fig. 19: π-π stacking interactions between bpydo ligands. All atoms shown in space filled representation.

Each of the layers of the 1D chain are able to stack on top of each other through the hydrogen bonds and the π-π stacking interactions. Each layer stacks on top of the layer below and is able to maintain areas where the uncoordinated molecules are able to reside (Fig. 20).

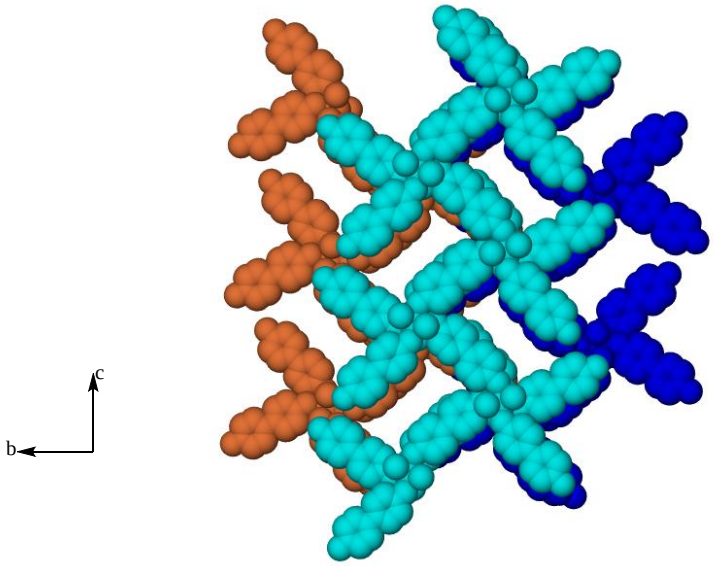


Fig. 20: Overlapping of 1D chains of $[Pr(bpydo)_4(H_2O)_3](ClO_4)_3 \cdot bpydo \cdot 5.5H_2O$. Each separate chain is a specific color, either orange, aqua, or blue.

The 1D chains are able to create a larger 3D structure through the interactions mentioned above. The structure is able to maintain space for the uncoordinated perchlorates, waters, and bpydo. The perchlorates and waters are shown sitting in these pores (Fig. 21).

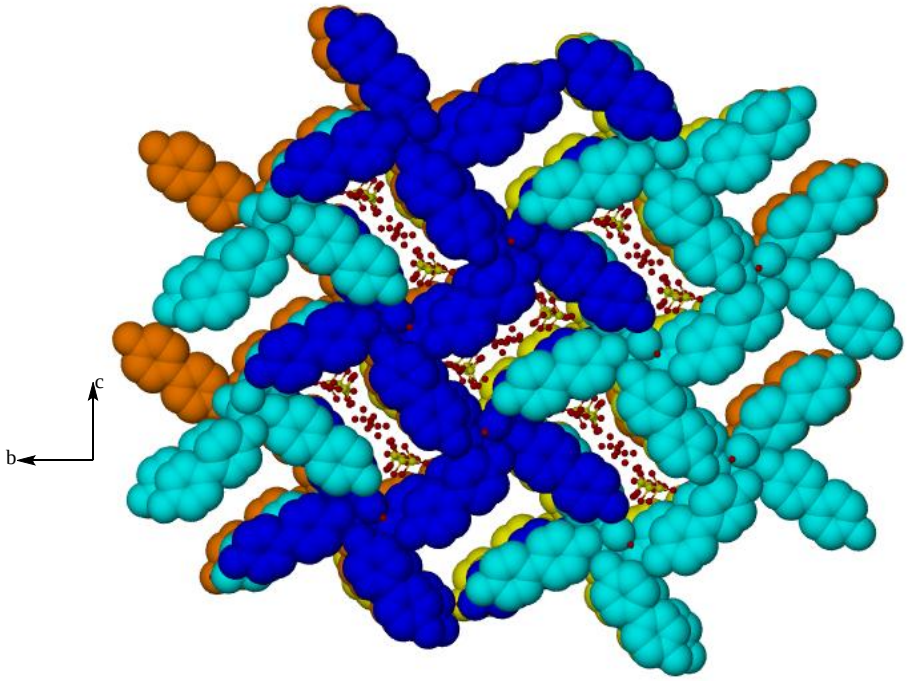
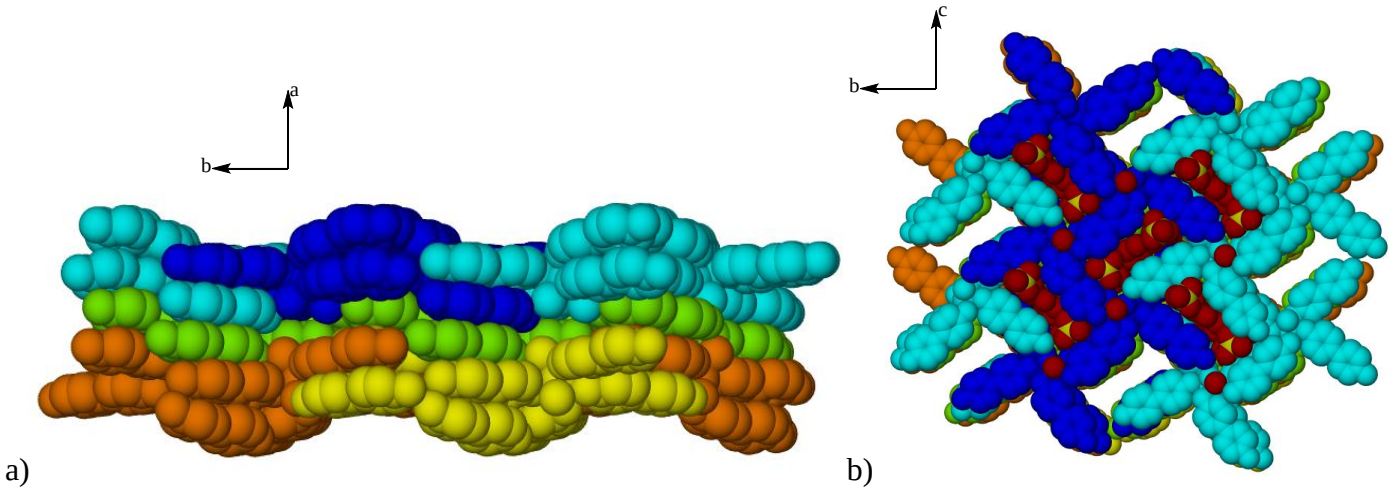


Fig. 21: View of the space-filled chains with the non-coordinated anions and waters in the pores. Each color, orange, aqua, blue, or yellow represents a different chain.

While it may seem that there is empty space in the pores for the uncoordinated ClO_4^{1-} and H_2O molecules, when their actual size is taken into account, the species completely fill the "free" area between the layers (Fig. 22).



a) b)

Fig. 22: A) Side view of the layers with the uncoordinated bpydo ligands in green. B) Top view of the layers with the perchlorate molecules, O=red and Cl=green/yellow, at van der Waal's radii in the "pores". Each separate chain is designated by different colors: orange, yellow, blue, or aqua.

Elemental analysis had been used to support our structure formula. The crystal analysis shows that the structure mass would be approximately the same (Appendix Table 1). The values analyzed for, however, are lower than the values that were found. If the results were within .4%, it would be acceptable. This could potentially be due to the noncoordinated waters. When the crystals are removed from water for elemental analysis, the compounds may not be stable, therefore, solvent may be lost that would change the found results. Since there is a significantly larger amount of carbon than other elements tested for, it would be easy to see if loss of water is causing the change. When different values were determined, it would seem that the noncoordinated water should be around 4.5 instead of 5.5 (Table 6).

Table 6: Analyzed for values with different water amounts for elemental.

If 5 noncoordinated H2O

	Element Mass	Total Mass	%C	%H	%N
Eu	151.964	1535.349	39.11164	3.676455	9.124963
Gd	157.25	1540.635	38.97744	3.663841	9.093654
Nd	144.24	1527.625	39.30939	3.695044	9.1711

If 4.5 noncoordinated H2O

	Element Mass	Total Mass	%C	%H	%N
Eu	151.964	1526.341	39.34245	3.631999	9.178813
Gd	157.25	1531.627	39.20667	3.619465	9.147135
Nd	144.24	1518.617	39.54255	3.650473	9.225499

If 3.5 noncoordinated H2O

	Element Mass	Total Mass	%C	%H	%N
Eu	151.964	1507.954	39.82217	3.518382	9.290734
Gd	157.25	1513.24	39.68306	3.506092	9.25828
Nd	144.24	1500.23	40.0272	3.536496	9.338568

If 3 noncoordinate H2O

	Element Mass	Total Mass	%C	%H	%N
Eu	151.964	1499.318	40.05154	3.495781	9.344249
Gd	157.25	1504.604	39.91083	3.4835	9.31142
Nd	144.24	1491.594	40.25894	3.513884	9.392636

If 2.5 noncoordinated H2O

	Element Mass	Total Mass	%C	%H	%N
Eu	151.964	1490.311	40.2936	3.449276	9.400722
Gd	157.25	1495.597	40.15119	3.437085	9.367497
Nd	144.24	1482.587	40.50353	3.467246	9.449698

Each of the structures formed are different from other structures currently published. Preliminary analysis of the other two structures generated indicate a 2D basket weave formation, compound **2**, and a 0D hydration complex of the metal, compound **3**. Compound **2** occurred for Tb, Dy, Ho, Er, and Yb. Er and Yb were the only two that formed compound **3**. This gives interesting separations in the lanthanide series. Previous research has differing trends for the series. Sun et al and Hill et al created structures using the lanthanide series that had the same topology for each..[20] Others, however, have found that there are changes that occur, potentially due to ionic radius size.[21, 25] It was proposed that, even though the change in radius is small, the steric

crowding around the metal was enough to cause a change in coordination. van Staveren et al believed that Sm was the pivotal metal for the change in structure.[21] Others have found there to be differences at Nd and then again at Eu.[25]

This research has found the changing points to occur at Tb and then again for Er and Yb. While this is different from what has been presented in the literature, this could be due to ligand choice. This does, however, cause a dispute with the research that has shown no change across the lanthanide series. Also, it can be concluded that the change in structures was not likely due to time. This can be said since the different concentrations afforded the same structures for the coordination networks.

Conclusions and Future Research

This research has discovered novel crystal coordination networks for the lanthanides with 4,4'-bipyridine-*N,N'*-dioxide. It has also determined a ratio of metal to ligand to solvent that was able to create the same structure in under 12 hours as compared to 2 months. Compound **1**, the focus of this research analysis, has been shown to occur in the lanthanide series from Pr to Tb. Compound **2**, the 2D basket weave, occurs for Lanthanides from Tb to Er. Compound **3**, the 0D hydration complex, was found to happen for Er and Yb. This has supported the idea of the affect of ionic radius on coordination complexes: as the radius decreases, the ability to bind ligands becomes more restricted.

Future work on this topic would be to complete an in depth structural analysis for compounds **2** and **3**. Also, the structures could be examined in other ways such as powder patterns and TGA to test the purity of the sample. It would also be interesting to see if the same pattern would occur for different N-oxide ligands that vary in size and bulkiness.

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Appendix

Table 1. Crystal data and structure refinement for Compound **1**

Empirical formula	C50 H56 Cl3 N10 O30.50 Pr
Formula weight	1532.31
Temperature	99(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 16.9538(11) A alpha = 90 deg. b = 21.2921(13) A beta = 109.7200(10) deg. c = 17.4278(11) A gamma = 90 deg.
Volume	5922.2(6) A^3
Z, Calculated density	4, 1.719 Mg/m^3
Absorption coefficient	1.063 mm^-1
F(000)	3120
Crystal size	0.33 x 0.24 x 0.19 mm
Theta range for data collection	1.28 to 30.51 deg.
Limiting indices	-24<=h<=24, -30<=k<=17, -24<=l<=24
Reflections collected / unique	42822 / 17699 [R(int) = 0.0533]
Completeness to theta = 30.51	97.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8236 and 0.7206
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	17699 / 212 / 995
Goodness-of-fit on F^2	1.022
Final R indices [I>2sigma(I)]	R1 = 0.0547, wR2 = 0.1226
R indices (all data)	R1 = 0.0791, wR2 = 0.1380
Largest diff. peak and hole	2.313 and -0.900 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for Compound **1**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Pr(1)	2478(1)	5127(1)	9905(1)	13(1)
Cl(1)	2361(1)	3699(1)	6582(1)	23(1)
Cl(2)	479(5)	6587(4)	3316(5)	17(1)
Cl(3)	4522(2)	6449(1)	3226(1)	18(1)
O(1)	3358(2)	4934(1)	11296(2)	20(1)
O(2)	4210(2)	1626(1)	15311(2)	22(1)
O(3)	2020(2)	4067(1)	10086(2)	17(1)
O(4)	1495(2)	166(1)	7109(2)	29(1)
O(5)	1021(2)	4972(1)	8913(2)	18(1)
O(6)	-417(2)	8097(1)	4630(2)	24(1)
O(7)	2558(2)	5350(1)	8554(2)	20(1)
O(8)	2015(2)	8787(1)	4779(1)	16(1)
O(9)	4643(2)	4566(1)	8889(2)	22(1)
O(10)	3767(2)	7953(1)	4958(2)	24(1)
O(11)	1552(2)	5251(1)	10707(2)	19(1)
O(12)	3493(2)	4432(1)	9632(2)	20(1)
O(13)	3752(2)	5811(1)	10279(2)	20(1)
O(14)	3011(2)	3913(2)	7292(2)	35(1)
O(15)	1566(2)	3938(2)	6582(2)	44(1)
O(16)	2503(2)	3907(2)	5854(2)	38(1)
O(17)	2328(2)	3021(1)	6582(2)	33(1)
O(18)	-74(9)	7110(8)	3303(13)	21(2)
O(19)	591(15)	6209(10)	4030(13)	37(4)
O(20)	146(15)	6226(11)	2582(12)	30(4)
O(21)	1293(6)	6848(4)	3359(7)	23(2)
O(22)	4048(8)	6971(4)	3385(8)	26(4)
O(23)	4747(5)	6032(3)	3892(4)	51(2)
O(24)	4041(8)	6147(7)	2481(5)	35(5)
O(25)	5273(3)	6704(3)	3136(4)	35(2)
N(1)	3465(2)	4485(1)	11846(2)	17(1)
N(2)	4111(2)	2074(2)	14761(2)	18(1)
N(3)	1984(2)	3543(1)	9666(2)	16(1)
N(4)	1602(2)	707(2)	7495(2)	20(1)
N(5)	704(2)	5369(2)	8291(2)	16(1)
N(6)	-234(2)	7660(1)	5195(2)	17(1)
N(7)	2487(2)	5821(1)	8040(2)	16(1)

N(8)	2060(2)	8321(1)	5300(2)	13(1)
N(9)	4543(2)	5026(1)	8351(2)	16(1)
N(10)	3916(2)	7495(1)	5499(2)	17(1)
C(1)	3520(2)	4640(2)	12616(2)	17(1)
C(2)	3655(2)	4174(2)	13200(2)	17(1)
C(3)	3732(2)	3541(2)	13012(2)	13(1)
C(4)	3678(2)	3412(2)	12205(2)	16(1)
C(5)	3552(2)	3881(2)	11647(2)	17(1)
C(6)	3914(2)	1934(2)	13963(2)	19(1)
C(7)	3787(2)	2402(2)	13395(2)	17(1)
C(8)	3870(2)	3036(2)	13620(2)	14(1)
C(9)	4091(2)	3165(2)	14454(2)	18(1)
C(10)	4208(2)	2681(2)	15008(2)	19(1)
C(11)	2164(2)	2990(2)	10071(2)	16(1)
C(12)	2131(2)	2437(2)	9652(2)	17(1)
C(13)	1896(2)	2433(2)	8799(2)	16(1)
C(14)	1711(2)	3014(2)	8403(2)	18(1)
C(15)	1765(2)	3562(2)	8843(2)	19(1)
C(16)	1572(2)	1254(2)	7096(2)	19(1)
C(17)	1671(2)	1818(2)	7502(2)	16(1)
C(18)	1814(2)	1835(2)	8343(2)	15(1)
C(19)	1856(2)	1259(2)	8738(2)	18(1)
C(20)	1747(2)	704(2)	8310(2)	20(1)
C(21)	615(2)	5185(2)	7524(2)	18(1)
C(22)	394(2)	5610(2)	6897(2)	18(1)
C(23)	260(2)	6243(2)	7037(2)	16(1)
C(24)	297(2)	6407(2)	7830(2)	16(1)
C(25)	500(2)	5959(2)	8439(2)	17(1)
C(26)	101(2)	7817(2)	5997(2)	18(1)
C(27)	274(2)	7363(2)	6598(2)	18(1)
C(28)	105(2)	6727(2)	6393(2)	17(1)
C(29)	-217(2)	6582(2)	5561(2)	17(1)
C(30)	-383(2)	7048(2)	4980(2)	20(1)
C(31)	2349(2)	5693(2)	7244(2)	17(1)
C(32)	2252(2)	6169(2)	6687(2)	15(1)
C(33)	2301(2)	6801(2)	6941(2)	16(1)
C(34)	2469(2)	6914(2)	7772(2)	18(1)
C(35)	2563(2)	6423(2)	8307(2)	18(1)
C(36)	2392(2)	8417(2)	6111(2)	19(1)
C(37)	2456(2)	7928(2)	6644(2)	19(1)
C(38)	2196(2)	7327(2)	6364(2)	16(1)
C(39)	1843(2)	7246(2)	5517(2)	17(1)
C(40)	1778(2)	7750(2)	4995(2)	16(1)
C(41)	4462(2)	4894(2)	7570(2)	20(1)
C(42)	4355(2)	5367(2)	7005(2)	18(1)
C(43)	4326(2)	5998(2)	7229(2)	17(1)

C(44)	4423(2)	6116(2)	8049(2)	19(1)
C(45)	4531(2)	5631(2)	8595(2)	20(1)
C(46)	4193(2)	7622(2)	6308(2)	18(1)
C(47)	4329(2)	7140(2)	6869(2)	18(1)
C(48)	4197(2)	6515(2)	6625(2)	16(1)
C(49)	3914(2)	6404(2)	5785(2)	20(1)
C(50)	3782(2)	6888(2)	5240(2)	21(1)
Cl(2B)	553(7)	6518(6)	3315(7)	38(3)
Cl(3B)	4369(4)	6370(3)	3298(4)	34(2)
O(18B)	93(12)	7076(10)	3346(16)	54(6)
O(19B)	482(13)	6085(9)	3914(12)	41(4)
O(20B)	233(16)	6250(13)	2522(12)	32(5)
O(21B)	1415(9)	6682(8)	3491(10)	68(5)
O(22B)	4099(14)	6988(8)	3374(16)	34(8)
O(23B)	4332(8)	5948(5)	3869(6)	42(3)
O(24B)	4057(11)	6147(11)	2473(9)	24(7)
O(25B)	5323(6)	6438(6)	3443(8)	54(4)
O(1W)	6(2)	5715(2)	230(2)	33(1)
O(2W)	692(8)	4810(5)	5390(5)	31(3)
O(3W)	1882(5)	5445(4)	4957(4)	32(2)
O(4W)	3186(4)	5247(3)	4392(4)	37(2)
O(5W)	3675(4)	4608(3)	5162(4)	39(2)
O(6W)	5150(5)	5020(4)	4895(5)	42(2)
O(7W)	2300(4)	5855(3)	12940(8)	50(3)
O(2WB)	1037(10)	4981(6)	5286(6)	43(4)
O(3WB)	2350(5)	5426(4)	4859(4)	52(2)
O(7WB)	2328(8)	5790(6)	13314(15)	57(5)

Table 3. Bond lengths [Å] and angles [deg] for Compound **1.**

Pr(1)-O(1)	2.414(3)	C(3)-C(8)	1.472(5)
Pr(1)-O(8)#1	2.428(2)	C(4)-C(5)	1.358(5)
Pr(1)-O(12)	2.436(3)	C(6)-C(7)	1.370(5)
Pr(1)-O(3)	2.442(2)	C(7)-C(8)	1.398(5)
Pr(1)-O(11)	2.443(2)	C(8)-C(9)	1.401(5)
Pr(1)-O(7)	2.450(2)	C(9)-C(10)	1.380(5)
Pr(1)-O(13)	2.501(3)	C(11)-C(12)	1.377(5)
Pr(1)-O(5)	2.514(3)	C(12)-C(13)	1.404(5)
Cl(1)-O(14)	1.425(3)	C(13)-C(14)	1.398(5)
Cl(1)-O(16)	1.439(3)	C(13)-C(18)	1.483(5)
Cl(1)-O(15)	1.442(3)	C(14)-C(15)	1.383(5)
Cl(1)-O(17)	1.445(3)	C(16)-C(17)	1.374(5)
Cl(2)-O(20)	1.434(15)	C(17)-C(18)	1.403(5)
Cl(2)-O(19)	1.439(17)	C(18)-C(19)	1.397(5)
Cl(2)-O(18)	1.451(14)	C(19)-C(20)	1.375(5)
Cl(2)-O(21)	1.467(12)	C(21)-C(22)	1.370(5)
Cl(3)-O(23)	1.409(6)	C(22)-C(23)	1.402(5)
Cl(3)-O(24)	1.430(8)	C(23)-C(24)	1.407(5)
Cl(3)-O(25)	1.439(5)	C(23)-C(28)	1.480(5)
Cl(3)-O(22)	1.453(8)	C(24)-C(25)	1.380(5)
O(1)-N(1)	1.321(4)	C(26)-C(27)	1.383(5)
O(2)-N(2)	1.323(4)	C(27)-C(28)	1.407(5)
O(3)-N(3)	1.326(4)	C(28)-C(29)	1.401(5)
O(4)-N(4)	1.315(4)	C(29)-C(30)	1.378(5)
O(5)-N(5)	1.336(4)	C(31)-C(32)	1.374(5)
O(6)-N(6)	1.314(4)	C(32)-C(33)	1.409(5)
O(7)-N(7)	1.322(4)	C(33)-C(34)	1.400(5)
O(8)-N(8)	1.330(3)	C(33)-C(38)	1.475(5)
O(8)-Pr(1)#2	2.428(2)	C(34)-C(35)	1.373(5)
O(9)-N(9)	1.327(4)	C(36)-C(37)	1.376(5)
O(10)-N(10)	1.320(4)	C(37)-C(38)	1.387(5)
N(1)-C(5)	1.354(5)	C(38)-C(39)	1.404(5)
N(1)-C(1)	1.355(4)	C(39)-C(40)	1.385(5)
N(2)-C(6)	1.350(4)	C(41)-C(42)	1.376(5)
N(2)-C(10)	1.353(5)	C(42)-C(43)	1.404(5)
N(3)-C(11)	1.354(4)	C(43)-C(44)	1.405(5)
N(3)-C(15)	1.355(5)	C(43)-C(48)	1.489(5)
N(4)-C(16)	1.350(5)	C(44)-C(45)	1.375(5)
N(4)-C(20)	1.357(5)	C(46)-C(47)	1.382(5)
N(5)-C(25)	1.351(5)	C(47)-C(48)	1.390(5)
N(5)-C(21)	1.352(4)	C(48)-C(49)	1.399(5)
N(6)-C(30)	1.355(5)	C(49)-C(50)	1.368(5)
N(6)-C(26)	1.361(5)	Cl(2B)-O(20B)	1.424(16)
N(7)-C(35)	1.356(5)	Cl(2B)-O(19B)	1.429(15)
N(7)-C(31)	1.356(4)	Cl(2B)-O(18B)	1.432(17)
N(8)-C(36)	1.349(4)	Cl(2B)-O(21B)	1.432(15)
N(8)-C(40)	1.349(4)	Cl(3B)-O(23B)	1.358(10)
N(9)-C(41)	1.350(5)	Cl(3B)-O(22B)	1.414(14)
N(9)-C(45)	1.359(5)	Cl(3B)-O(24B)	1.434(13)
N(10)-C(46)	1.354(5)	Cl(3B)-O(25B)	1.557(11)
N(10)-C(50)	1.362(5)	O(6W)-O(6W)#3	0.727(11)
C(1)-C(2)	1.385(5)	O(1)-Pr(1)-O(8)#1	108.98(9)
C(2)-C(3)	1.404(5)	O(1)-Pr(1)-O(12)	81.67(9)
C(3)-C(4)	1.405(4)	O(8)#1-Pr(1)-O(12)	142.13(9)

O(1)-Pr(1)-O(3)	80.12(9)	C(16)-N(4)-C(20)	120.3(3)
O(8)#1-Pr(1)-O(3)	141.68(8)	O(5)-N(5)-C(25)	119.6(3)
O(12)-Pr(1)-O(3)	74.92(9)	O(5)-N(5)-C(21)	119.8(3)
O(1)-Pr(1)-O(11)	75.11(9)	C(25)-N(5)-C(21)	120.5(3)
O(8)#1-Pr(1)-O(11)	72.46(8)	O(6)-N(6)-C(30)	119.9(3)
O(12)-Pr(1)-O(11)	144.12(9)	O(6)-N(6)-C(26)	120.4(3)
O(3)-Pr(1)-O(11)	74.44(9)	C(30)-N(6)-C(26)	119.7(3)
O(1)-Pr(1)-O(7)	141.48(9)	O(7)-N(7)-C(35)	120.6(3)
O(8)#1-Pr(1)-O(7)	81.32(8)	O(7)-N(7)-C(31)	119.1(3)
O(12)-Pr(1)-O(7)	70.00(9)	C(35)-N(7)-C(31)	120.3(3)
O(3)-Pr(1)-O(7)	115.22(9)	O(8)-N(8)-C(36)	120.7(3)
O(11)-Pr(1)-O(7)	141.54(9)	O(8)-N(8)-C(40)	118.2(3)
O(1)-Pr(1)-O(13)	69.63(9)	C(36)-N(8)-C(40)	121.1(3)
O(8)#1-Pr(1)-O(13)	72.16(9)	O(9)-N(9)-C(41)	120.2(3)
O(12)-Pr(1)-O(13)	78.48(9)	O(9)-N(9)-C(45)	119.3(3)
O(3)-Pr(1)-O(13)	142.09(9)	C(41)-N(9)-C(45)	120.4(3)
O(11)-Pr(1)-O(13)	116.98(9)	O(10)-N(10)-C(46)	120.8(3)
O(7)-Pr(1)-O(13)	79.32(9)	O(10)-N(10)-C(50)	119.6(3)
O(1)-Pr(1)-O(5)	143.03(8)	C(46)-N(10)-C(50)	119.6(3)
O(8)#1-Pr(1)-O(5)	81.38(8)	N(1)-C(1)-C(2)	119.5(3)
O(12)-Pr(1)-O(5)	112.33(9)	C(1)-C(2)-C(3)	121.5(3)
O(3)-Pr(1)-O(5)	71.67(8)	C(2)-C(3)-C(4)	116.2(3)
O(11)-Pr(1)-O(5)	74.66(9)	C(2)-C(3)-C(8)	122.5(3)
O(7)-Pr(1)-O(5)	73.98(8)	C(4)-C(3)-C(8)	121.3(3)
O(13)-Pr(1)-O(5)	144.78(8)	C(5)-C(4)-C(3)	121.0(3)
O(14)-Cl(1)-O(16)	110.9(2)	N(1)-C(5)-C(4)	121.2(3)
O(14)-Cl(1)-O(15)	109.6(2)	N(2)-C(6)-C(7)	120.4(3)
O(16)-Cl(1)-O(15)	109.0(2)	C(6)-C(7)-C(8)	121.6(3)
O(14)-Cl(1)-O(17)	109.82(19)	C(7)-C(8)-C(9)	116.6(3)
O(16)-Cl(1)-O(17)	108.95(19)	C(7)-C(8)-C(3)	121.8(3)
O(15)-Cl(1)-O(17)	108.5(2)	C(9)-C(8)-C(3)	121.7(3)
O(20)-Cl(2)-O(19)	111.7(9)	C(10)-C(9)-C(8)	120.2(3)
O(20)-Cl(2)-O(18)	109.8(8)	N(2)-C(10)-C(9)	121.2(3)
O(19)-Cl(2)-O(18)	109.7(8)	N(3)-C(11)-C(12)	120.4(3)
O(20)-Cl(2)-O(21)	109.2(8)	C(11)-C(12)-C(13)	120.8(3)
O(19)-Cl(2)-O(21)	108.7(8)	C(14)-C(13)-C(12)	117.0(3)
O(18)-Cl(2)-O(21)	107.5(7)	C(14)-C(13)-C(18)	122.0(3)
O(23)-Cl(3)-O(24)	112.2(6)	C(12)-C(13)-C(18)	120.9(3)
O(23)-Cl(3)-O(25)	108.9(4)	C(15)-C(14)-C(13)	120.7(3)
O(24)-Cl(3)-O(25)	109.0(5)	N(3)-C(15)-C(14)	120.3(3)
O(23)-Cl(3)-O(22)	109.8(5)	N(4)-C(16)-C(17)	120.8(3)
O(24)-Cl(3)-O(22)	109.5(6)	C(16)-C(17)-C(18)	120.6(3)
O(25)-Cl(3)-O(22)	107.4(5)	C(19)-C(18)-C(17)	117.0(3)
N(1)-O(1)-Pr(1)	137.6(2)	C(19)-C(18)-C(13)	120.7(3)
N(3)-O(3)-Pr(1)	131.7(2)	C(17)-C(18)-C(13)	122.3(3)
N(5)-O(5)-Pr(1)	120.53(19)	C(20)-C(19)-C(18)	120.8(3)
N(7)-O(7)-Pr(1)	140.9(2)	N(4)-C(20)-C(19)	120.5(3)
N(8)-O(8)-Pr(1)#2	134.9(2)	N(5)-C(21)-C(22)	120.4(3)
O(1)-N(1)-C(5)	120.1(3)	C(21)-C(22)-C(23)	121.0(3)
O(1)-N(1)-C(1)	119.2(3)	C(22)-C(23)-C(24)	116.9(3)
C(5)-N(1)-C(1)	120.6(3)	C(22)-C(23)-C(28)	122.4(3)
O(2)-N(2)-C(6)	120.9(3)	C(24)-C(23)-C(28)	120.7(3)
O(2)-N(2)-C(10)	119.1(3)	C(25)-C(24)-C(23)	120.1(3)
C(6)-N(2)-C(10)	120.0(3)	N(5)-C(25)-C(24)	120.6(3)
O(3)-N(3)-C(11)	118.9(3)	N(6)-C(26)-C(27)	120.9(3)
O(3)-N(3)-C(15)	120.3(3)	C(26)-C(27)-C(28)	120.5(3)
C(11)-N(3)-C(15)	120.8(3)	C(29)-C(28)-C(27)	116.8(3)
O(4)-N(4)-C(16)	121.2(3)	C(29)-C(28)-C(23)	122.6(3)
O(4)-N(4)-C(20)	118.5(3)	C(27)-C(28)-C(23)	120.6(3)

C(30)-C(29)-C(28)	120.9(3)	C(45)-C(44)-C(43)	120.8(4)
N(6)-C(30)-C(29)	121.1(3)	N(9)-C(45)-C(44)	120.5(3)
N(7)-C(31)-C(32)	120.8(3)	N(10)-C(46)-C(47)	120.3(3)
C(31)-C(32)-C(33)	120.2(3)	C(46)-C(47)-C(48)	121.5(3)
C(34)-C(33)-C(32)	117.3(3)	C(47)-C(48)-C(49)	116.4(3)
C(34)-C(33)-C(38)	120.7(3)	C(47)-C(48)-C(43)	121.5(3)
C(32)-C(33)-C(38)	122.1(3)	C(49)-C(48)-C(43)	122.1(3)
C(35)-C(34)-C(33)	120.6(3)	C(50)-C(49)-C(48)	121.1(4)
N(7)-C(35)-C(34)	120.7(3)	N(10)-C(50)-C(49)	121.0(3)
N(8)-C(36)-C(37)	120.2(3)	O(20B)-Cl(2B)-O(19B)	110.6(9)
C(36)-C(37)-C(38)	121.2(3)	O(20B)-Cl(2B)-O(18B)	109.7(9)
C(37)-C(38)-C(39)	117.1(3)	O(19B)-Cl(2B)-O(18B)	109.1(9)
C(37)-C(38)-C(33)	120.6(3)	O(20B)-Cl(2B)-O(21B)	109.5(9)
C(39)-C(38)-C(33)	122.3(3)	O(19B)-Cl(2B)-O(21B)	109.4(9)
C(40)-C(39)-C(38)	120.4(3)	O(18B)-Cl(2B)-O(21B)	108.6(9)
N(8)-C(40)-C(39)	120.0(3)	O(23B)-Cl(3B)-O(22B)	116.7(10)
N(9)-C(41)-C(42)	120.8(4)	O(23B)-Cl(3B)-O(24B)	115.1(9)
C(41)-C(42)-C(43)	120.6(3)	O(22B)-Cl(3B)-O(24B)	112.4(10)
C(42)-C(43)-C(44)	116.8(3)	O(23B)-Cl(3B)-O(25B)	104.1(6)
C(42)-C(43)-C(48)	121.5(3)	O(22B)-Cl(3B)-O(25B)	104.4(9)
C(44)-C(43)-C(48)	121.7(3)	O(24B)-Cl(3B)-O(25B)	101.9(8)

Symmetry transformations used to generate equivalent atoms:
#1 x,-y+3/2,z+1/2 #2 x,-y+3/2,z-1/2
#3 -x+1,-y+1,-z+1

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for Compound **1**.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Pr(1)	15(1)	10(1)	13(1)	1(1)	4(1)	1(1)
Cl(1)	26(1)	23(1)	18(1)	0(1)	4(1)	-3(1)
Cl(2)	20(2)	14(2)	14(2)	0(1)	4(1)	-1(1)
Cl(3)	19(1)	21(1)	12(1)	-1(1)	2(1)	-2(1)
O(1)	24(1)	18(1)	12(1)	6(1)	0(1)	-2(1)
O(2)	31(2)	17(1)	15(1)	6(1)	4(1)	-5(1)
O(3)	24(1)	8(1)	20(1)	-1(1)	7(1)	0(1)
O(4)	50(2)	18(2)	23(2)	-9(1)	16(1)	-8(1)
O(5)	18(1)	18(1)	15(1)	6(1)	2(1)	1(1)
O(6)	32(2)	19(2)	18(1)	7(1)	4(1)	3(1)
O(7)	29(1)	16(1)	15(1)	5(1)	7(1)	0(1)
O(8)	23(1)	12(1)	13(1)	4(1)	5(1)	0(1)
O(9)	24(1)	20(2)	23(1)	9(1)	9(1)	2(1)
O(10)	35(2)	15(1)	21(1)	2(1)	9(1)	2(1)
O(11)	21(1)	21(2)	16(1)	3(1)	10(1)	1(1)
O(12)	26(1)	14(1)	24(1)	6(1)	14(1)	6(1)
O(13)	18(1)	13(1)	23(1)	4(1)	2(1)	-2(1)
O(14)	37(2)	36(2)	23(2)	-6(1)	-1(1)	-11(1)
O(15)	29(2)	53(2)	51(2)	-8(2)	12(2)	6(2)
O(16)	58(2)	36(2)	22(2)	4(1)	15(2)	-6(2)
O(17)	44(2)	19(2)	29(2)	3(1)	5(1)	-6(1)
O(18)	24(3)	14(5)	26(5)	1(3)	10(3)	4(3)
O(19)	61(9)	22(7)	28(7)	3(5)	15(6)	8(5)
O(20)	41(6)	19(6)	30(8)	-4(5)	12(6)	-7(5)
O(21)	19(3)	16(3)	31(4)	-6(3)	3(3)	4(3)
O(22)	42(6)	19(4)	18(4)	-4(2)	10(3)	7(2)
O(23)	52(2)	48(2)	48(2)	4(1)	14(1)	1(1)
O(24)	44(7)	23(5)	23(5)	-7(2)	-8(2)	3(2)
O(25)	34(2)	36(2)	36(2)	-2(1)	13(1)	-1(1)
N(1)	14(1)	16(2)	16(2)	4(1)	1(1)	-2(1)
N(2)	21(2)	16(2)	16(2)	3(1)	5(1)	-3(1)
N(3)	16(1)	14(2)	17(2)	-1(1)	5(1)	-1(1)
N(4)	24(2)	19(2)	18(2)	-4(1)	8(1)	-4(1)
N(5)	16(1)	16(2)	15(2)	4(1)	2(1)	0(1)
N(6)	19(2)	14(2)	17(2)	2(1)	6(1)	2(1)
N(7)	18(1)	16(2)	14(1)	3(1)	6(1)	-2(1)
N(8)	14(1)	12(1)	12(1)	2(1)	3(1)	0(1)
N(9)	14(1)	18(2)	17(2)	4(1)	5(1)	-1(1)
N(10)	20(2)	15(2)	17(2)	3(1)	6(1)	1(1)
C(1)	19(2)	17(2)	16(2)	1(1)	5(1)	-1(1)
C(2)	20(2)	19(2)	12(2)	0(1)	4(1)	-1(1)
C(3)	14(2)	14(2)	12(2)	1(1)	4(1)	0(1)
C(4)	17(2)	19(2)	12(2)	1(1)	4(1)	3(1)
C(5)	18(2)	21(2)	11(2)	-1(1)	3(1)	1(1)
C(6)	26(2)	15(2)	16(2)	1(1)	7(2)	0(2)
C(7)	24(2)	15(2)	12(2)	-3(1)	7(1)	-2(1)
C(8)	12(2)	15(2)	14(2)	-1(1)	3(1)	-1(1)
C(9)	26(2)	15(2)	12(2)	-1(1)	3(1)	-3(1)

C(10)	26(2)	17(2)	12(2)	0(1)	2(1)	-5(2)
C(11)	15(2)	15(2)	16(2)	4(1)	3(1)	0(1)
C(12)	20(2)	12(2)	20(2)	3(1)	7(1)	3(1)
C(13)	12(2)	16(2)	17(2)	-1(1)	3(1)	0(1)
C(14)	21(2)	16(2)	15(2)	2(1)	5(1)	1(1)
C(15)	21(2)	14(2)	20(2)	5(1)	4(1)	1(1)
C(16)	18(2)	24(2)	14(2)	2(1)	3(1)	-1(2)
C(17)	18(2)	14(2)	18(2)	-1(1)	7(1)	-1(1)
C(18)	15(2)	11(2)	20(2)	-1(1)	7(1)	1(1)
C(19)	23(2)	16(2)	15(2)	-1(1)	6(1)	0(1)
C(20)	28(2)	15(2)	20(2)	2(1)	11(2)	2(2)
C(21)	19(2)	15(2)	16(2)	1(1)	3(1)	2(1)
C(22)	23(2)	14(2)	15(2)	1(1)	5(1)	0(1)
C(23)	14(2)	16(2)	16(2)	1(1)	2(1)	-1(1)
C(24)	17(2)	16(2)	15(2)	1(1)	4(1)	1(1)
C(25)	15(2)	18(2)	17(2)	1(1)	4(1)	1(1)
C(26)	19(2)	13(2)	20(2)	0(1)	5(1)	1(1)
C(27)	19(2)	15(2)	20(2)	1(1)	7(1)	1(1)
C(28)	15(2)	16(2)	18(2)	1(1)	5(1)	2(1)
C(29)	18(2)	12(2)	18(2)	-3(1)	4(1)	1(1)
C(30)	21(2)	21(2)	14(2)	-1(1)	2(1)	1(2)
C(31)	18(2)	16(2)	16(2)	-3(1)	6(1)	-1(1)
C(32)	17(2)	17(2)	9(2)	1(1)	1(1)	-3(1)
C(33)	14(2)	15(2)	17(2)	2(1)	5(1)	0(1)
C(34)	22(2)	13(2)	19(2)	1(1)	7(1)	-1(1)
C(35)	22(2)	17(2)	14(2)	-1(1)	5(1)	-4(1)
C(36)	21(2)	14(2)	18(2)	-2(1)	2(1)	1(1)
C(37)	23(2)	19(2)	12(2)	-3(1)	2(1)	-2(2)
C(38)	14(2)	16(2)	16(2)	2(1)	3(1)	1(1)
C(39)	20(2)	15(2)	15(2)	0(1)	5(1)	-3(1)
C(40)	21(2)	16(2)	12(2)	0(1)	4(1)	0(1)
C(41)	24(2)	17(2)	20(2)	-1(2)	9(2)	2(2)
C(42)	20(2)	18(2)	17(2)	0(1)	7(1)	2(2)
C(43)	13(2)	21(2)	18(2)	1(1)	7(1)	1(1)
C(44)	17(2)	18(2)	21(2)	2(1)	5(1)	1(1)
C(45)	19(2)	24(2)	17(2)	3(1)	5(1)	-1(2)
C(46)	19(2)	15(2)	20(2)	-3(1)	6(1)	-1(1)
C(47)	19(2)	15(2)	20(2)	-4(1)	6(1)	0(1)
C(48)	18(2)	13(2)	16(2)	0(1)	5(1)	1(1)
C(49)	23(2)	16(2)	21(2)	-1(1)	7(2)	0(2)
C(50)	27(2)	18(2)	16(2)	0(1)	5(2)	1(2)
Cl(2B)	58(5)	30(4)	31(3)	-8(2)	22(3)	-5(3)
O(18B)	100(15)	31(8)	47(10)	9(6)	47(11)	11(9)
O(19B)	58(7)	40(9)	27(6)	12(6)	16(5)	12(6)
O(20B)	51(10)	31(9)	14(6)	-7(5)	8(6)	-9(6)
O(21B)	52(7)	88(9)	69(8)	-24(7)	24(6)	-36(6)
O(1W)	25(2)	20(2)	57(2)	5(2)	19(2)	3(1)
O(2W)	34(5)	29(4)	33(4)	-9(3)	15(3)	-5(4)
O(3W)	25(4)	44(5)	24(4)	-5(3)	6(3)	-1(3)
O(4W)	40(3)	37(4)	38(4)	-16(3)	17(3)	-9(3)
O(5W)	48(4)	36(4)	37(3)	-9(3)	21(3)	-11(3)
O(6W)	34(4)	52(4)	41(4)	25(3)	15(3)	12(3)
O(7W)	50(3)	51(3)	50(3)	0(1)	17(1)	0(1)
O(2WB)	34(7)	46(6)	40(4)	8(4)	3(4)	9(5)
O(3WB)	52(3)	52(3)	52(3)	-2(1)	17(1)	0(1)
O(7WB)	57(5)	57(5)	57(5)	0(1)	19(2)	-1(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for Compound **1**.

	x	y	z	U(eq)
H(1)	3466	5066	12754	21
H(2)	3697	4285	13740	21
H(4)	3730	2992	12047	20
H(5)	3525	3782	11107	21
H(6)	3864	1507	13794	23
H(7)	3639	2294	12836	20
H(9)	4161	3588	14640	22
H(10)	4361	2775	15572	23
H(11)	2315	2983	10648	19
H(12)	2270	2052	9944	20
H(14)	1547	3032	7826	21
H(15)	1649	3954	8567	23
H(16)	1481	1250	6528	23
H(17)	1643	2199	7211	20
H(19)	1962	1250	9309	21
H(20)	1774	316	8588	24
H(21)	707	4758	7419	21
H(22)	330	5474	6361	21
H(24)	183	6826	7947	19
H(25)	496	6068	8967	20
H(26)	218	8245	6145	21
H(29)	-323	6156	5394	20
H(30)	-605	6939	4419	23
H(31)	2320	5268	7068	20
H(32)	2152	6072	6130	18
H(34)	2518	7333	7968	22
H(35)	2683	6507	8871	21
H(36)	2582	8824	6315	22
H(37)	2683	8003	7214	23
H(39)	1649	6843	5299	20
H(40)	1534	7692	4423	20
H(41)	4480	4470	7408	24
H(42)	4301	5265	6459	22
H(44)	4415	6537	8228	23
H(45)	4597	5719	9148	24
H(46)	4294	8044	6491	22
H(47)	4518	7237	7434	22
H(49)	3812	5985	5589	24
H(50)	3594	6800	4673	25
H(11A)	1590(20)	5059(14)	11130(15)	0(8)
H(12A)	3730(20)	4105(12)	9850(20)	10(10)
H(13A)	3770(30)	6201(9)	10240(30)	43(15)
H(11B)	1050(13)	5355(18)	10530(20)	11(10)
H(12B)	3800(20)	4510(20)	9350(20)	34(13)
H(13B)	4210(20)	5640(20)	10560(30)	51(17)
H(1WA)	-340(20)	5550(20)	400(30)	30(13)
H(1WB)	-230(30)	6056(14)	70(30)	37(15)

Table 6. Hydrogen bonds for Compound 1 [Å and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(12)-H(12A)...O(2)#4	0.833(18)	1.809(19)	2.641(4)	177(4)
O(12)-H(12B)...O(9)	0.845(19)	1.87(2)	2.696(3)	167(5)
O(11)-H(11A)...O(4)#5	0.827(18)	1.83(2)	2.632(4)	163(3)
O(11)-H(11B)...O(1W)#6	0.832(18)	1.84(2)	2.658(4)	170(4)
O(13)-H(13B)...O(9)#7	0.85(2)	1.90(2)	2.737(4)	166(5)
O(13)-H(13A)...O(10)#1	0.835(19)	1.87(2)	2.693(4)	170(5)
O(1W)-H(1WA)...O(5)#8	0.828(19)	2.21(2)	3.027(4)	168(4)
O(1W)-H(1WB)...O(6)#2	0.831(19)	1.94(3)	2.738(4)	161(5)

Symmetry transformations used to generate equivalent atoms:
#1 x,-y+3/2,z+1/2 #2 x,-y+3/2,z-1/2 #3 -x+1,-y+1,-z+1
#4 x,-y+1/2,z-1/2 #5 x,-y+1/2,z+1/2 #6 x,y,z+1
#7 -x+1,-y+1,-z+2 #8 -x,-y+1,-z+1