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Supporting information for article:

**Isomorphous rare-earth bis[bis(2,6-diisopropylphenyl)phosphate]
complexes and their self-assembly into a two-dimensional
framework by intramolecular hydrogen bonds**

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S1. Solid state NMR and IR studies

S1.1. ^{31}P CP MAS NMR studies

^{31}P CP-MAS NMR spectra of (3) were registered on a Varian Unity Inova AS500 instrument (with working frequency of 500 MHz). The used rotor speeds were 4.2 and 5.4 kHz.

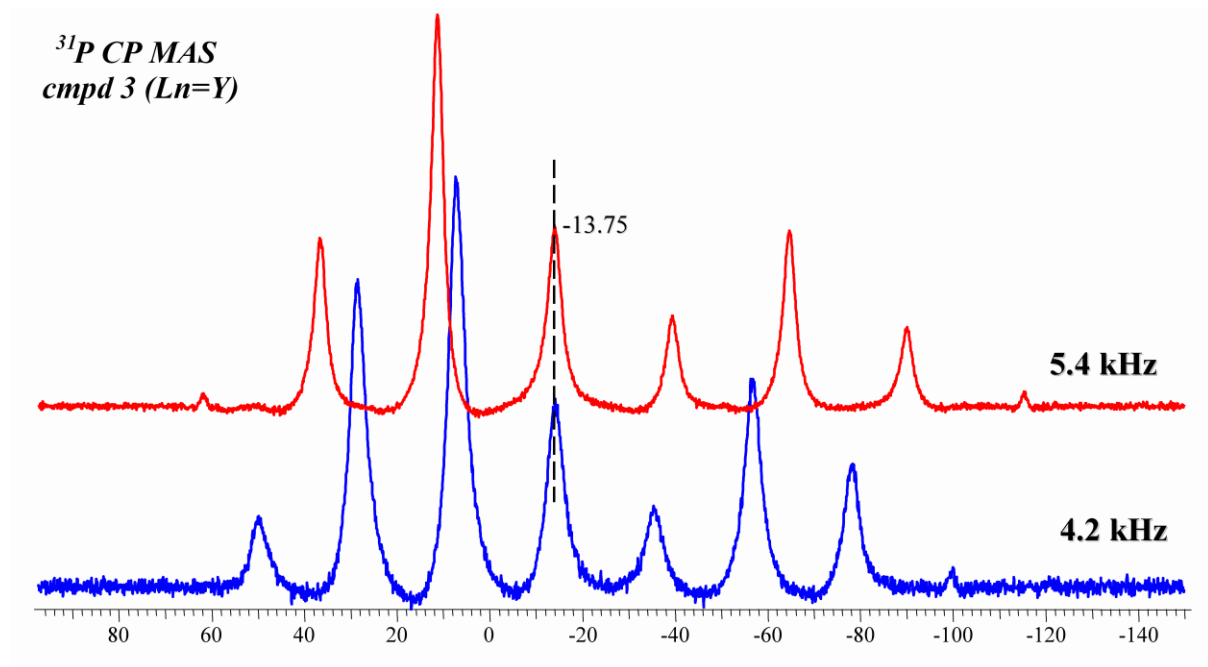


Figure S1 ^{31}P CP MAS NMR spectra of (3).

Solid state ^{31}P CP MAS NMR spectra of microcrystalline (3) at different rotation frequencies demonstrate signals that correspond to only one symmetrically nonequivalent phosphorous center.

S1.2. ATR-FTIR studies

The attenuated total reflectance (ATR) fourier transform infrared (FTIR) spectra of (1), (2) and (4) were recorded with the "HYPERION-2000" IR microscope connected to the "IFS 66 v/s Bruker" FTIR spectrometer (Ge crystal, 2 cm^{-1} resolution, 150 scans, $600\text{--}4000\text{ cm}^{-1}$ wavenumber range).

According to IR data of (1) and (3), the presence of MeOH, $[\text{OOP}(\text{O}-2,6\text{-iPr}_2\text{C}_6\text{H}_3)_2]$ ligands and framework of hydrogen ($\text{OH}\dots\text{O}$) bonding has been confirmed. Compounds (1) and (3) are isostructural. Slightly different amount of methanol is due to different time of drying under vacuum.

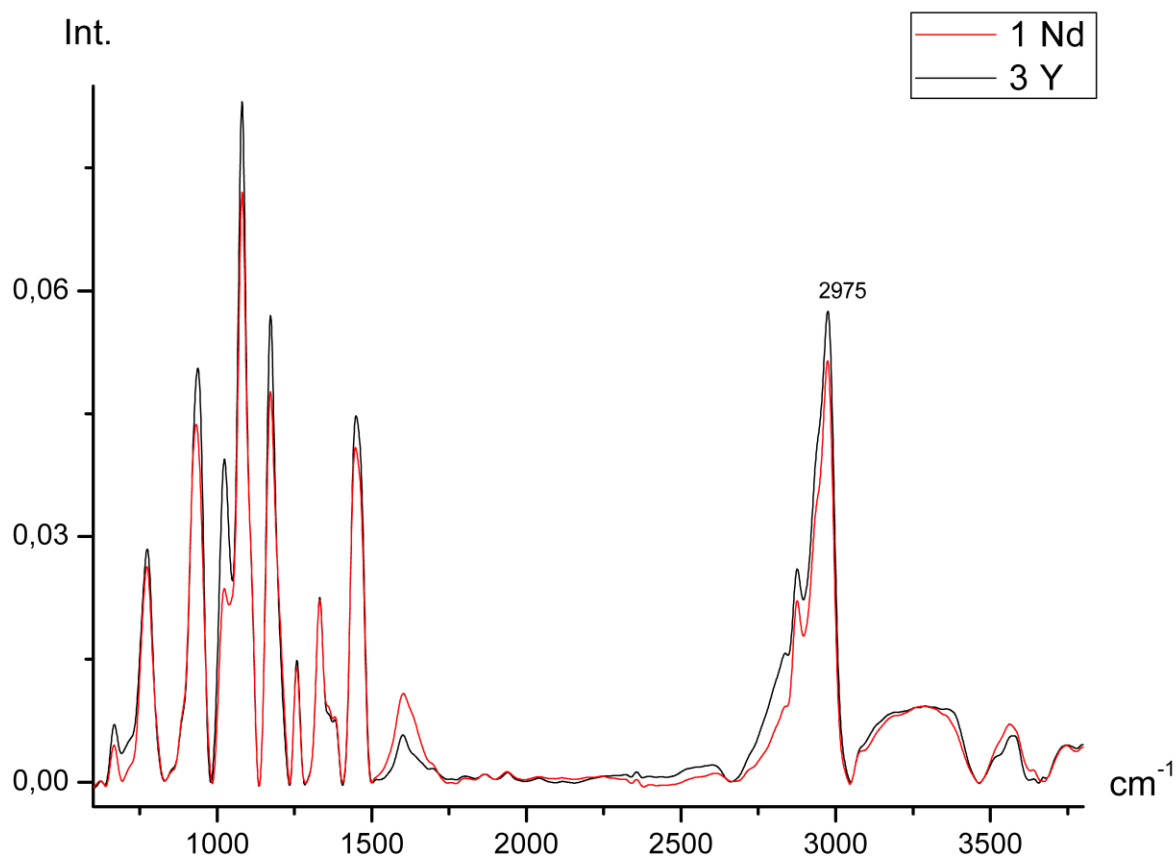


Figure S2 The ATR-FTIR spectra of (1) (Ln=Nd, red line) and (3) (Ln=Y, black line).

Table S1 Assignment of some absorption bands and their maxima in IR spectra of (1) and (3).

Cmpd.	ⁱ Pr, $\nu(\text{cm}^{-1})$	Ph, $\nu(\text{cm}^{-1})$	P-O, C-O Ph, cm^{-1}	MeOH, cm^{-1}
	$\nu_{\text{CH}} / \delta_{\text{CCH}}$	$\nu_{\text{CH}} / \nu_{\text{CC}} / \delta_{\text{CCH}}$	ν / δ	ν_{COH}
(1)	2974, 2874 / 1449	3081 / 1602 / 775	1174, 1081 / 933	3563, 3284, 1640, 1025sh
(3)	2974, 2874 / 1449	3081 / 1602 / 775	1174, 1081 / 939	3576, 3522, 3366, 1025

The ATR-FTIR spectrum of (4) exhibits the presence of MeOH, the organophosphate [OOP(O-2,6-ⁱPr₂C₆H₃)₂] and nitrate anions, and the presence of hydrogen (OH...O) bonds.

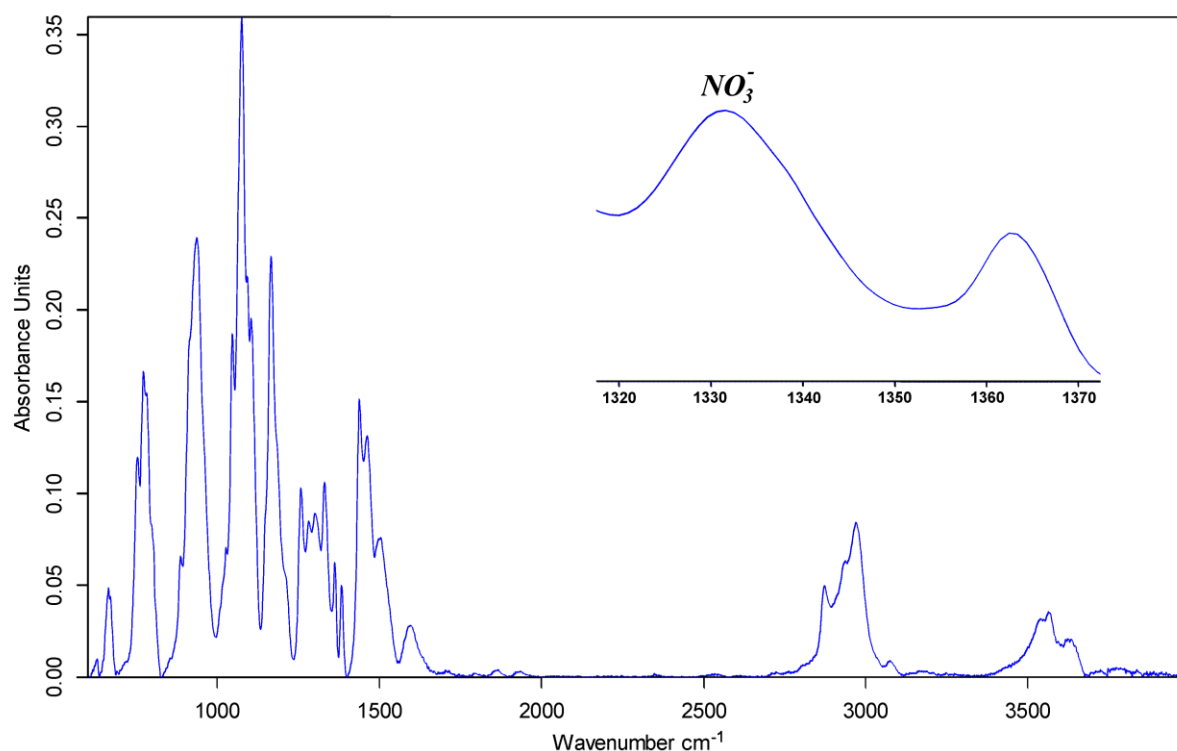


Figure S3 The ATR-FTIR spectrum of (4)

S1.3. Elemental C/H analysis for (1) and (3)

Table S2 Theoretical and experimental C/H content (%) in $\text{LnCl}[\text{O}_2\text{P}(\text{O}-2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)_2]_2(\text{CH}_3\text{OH})_x$

Cmpd	Element	Cald. for x=4	Cald. for x=5	Cald. for x=6	Experimental
(1)	C	54.65	54.18	53.74	54.01
Ln=Nd	H	7.41	7.55	7.68	7.58
(3)	C	57.43	56.86	56.32	56.61
Ln=Y	H	7.79	7.92	8.05	7.90

S2. Additional refinement details

S2.1. Modeling methanol disorder in (1)

Carbon and oxygen atoms of the non-coordinating and one coordinated methanol molecules exhibit relatively large thermal ellipsoid in crystallographic models of (2), (3) and especially (1), which might be attributed to a minor disorder of methanol molecules. We have chosen complex $\{\text{Nd}[\text{O}_2\text{P}(\text{O}-2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)_2]_2\text{Cl}(\text{CH}_3\text{OH})_4\}(\text{CH}_3\text{OH})_2$ (1) for modeling the methanol disorder. We have

found that two methanol molecules (atoms O6-C26, O7-C27) might be disordered over two positions for each. However, the SHELXL (Sheldrick, 2015) program has not detected that these atoms have to be split. The disorder has been resolved by using 28 SHELXL restraints: ISOR, EADP DFIX and AFIX SHELXL instructions. Since positions of H29, H29', H30 and H30' atoms (Fig. S4) had to be fixed with the AFIX 3 instruction, parameters for corresponding H-bonds are not quite accurate and do not have the ESDs. Changed model parameters are the following: number of parameters, restraints — 353, 28; $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S — 0.0351, 0.0896, 1.054; $\Delta\rho_{\max}$, $\Delta\rho_{\min}$ — 1.561, -0.949. The occupancy ratios are 0.551(16):0.449(16) for (O6-C26) and (O6'-C26') positions and 0.559(12):0.441(12) for (O7-C27) and (O7'-C27') positions, correspondingly (Fig. S4). The modeling allowed to eliminate four following level C Alerts from the checkCIF/PLATON report:

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PLAT220_ALERT_2_C Large Non-Solvent C   Ueq(max)/Ueq(min) Range    5.7 Ratio
PLAT220_ALERT_2_C Large Non-Solvent O   Ueq(max)/Ueq(min) Range    3.4 Ratio
PLAT222_ALERT_3_C Large Non-Solvent H   Uiso(max)/Uiso(min) ...    5.9 Ratio
PLAT975_ALERT_2_C Check Calcd Residual Density 0.92A From   O7    0.58 eA-3

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However, this disorder has not been included in the final crystallographic model due to inaccurate description of H-bonding and due to an unreasonably large number of used restraints for two MeOH molecules.

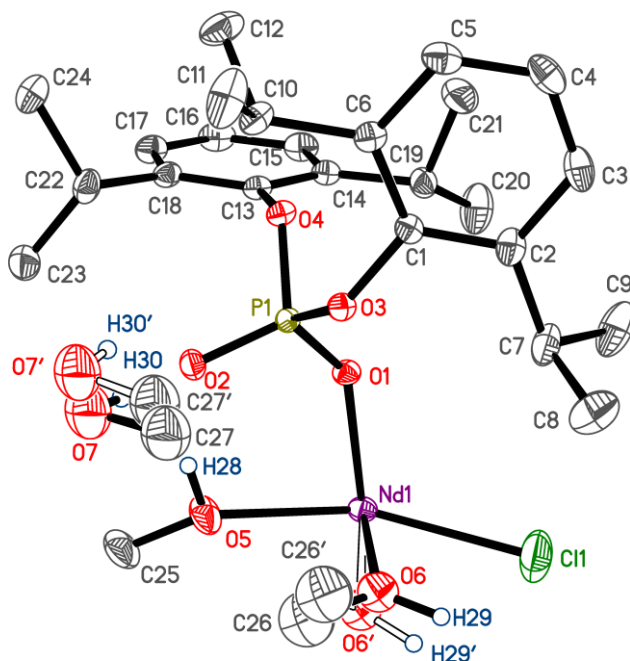


Figure S4 The asymmetric unit and disordered fragments in (1). Occupancies of Cl1 and Nd1 atoms are 50%. Only hydroxy H atoms are shown. Displacement ellipsoids for non-H atoms are drawn at 50% probability level. The second components of disorder are shown with a solid open line.

S2.2. Disorder in (4).

The asymmetric unit of $\{\text{Nd}[\text{O}_2\text{P}(\text{O}-2,6\text{-iPr}_2\text{C}_6\text{H}_3)_2]_2(\text{NO}_3)(\text{CH}_3\text{OH})_4\}(\text{CH}_3\text{OH})_2$, (4), is shown on Fig. S5. The non-coordinating methanol molecule is disordered over 2 positions (non-H atoms O7, C27 and O7', C7'). Carbon atoms of two coordinated methanol molecules are also disordered over two positions (atoms C25, C25' and C26, C26'). One of *iso*-propyl group is disordered over 2 positions (atoms C11, C12 and C11', C12'). The NO_3^- anion is disordered over two-fold rotation axis with 50% occupancies for N1, O8, O9 and O10 atoms, which symmetrical equivalents are generated with the following symmetry operation: $-x+1, y, -z+1/2$. Atoms N1 and O10 are located nearly on the axis. Atom C27 demonstrates high displacements U parameters, and its position may be split into two positions, but this was not modeled (see also section S2.1).

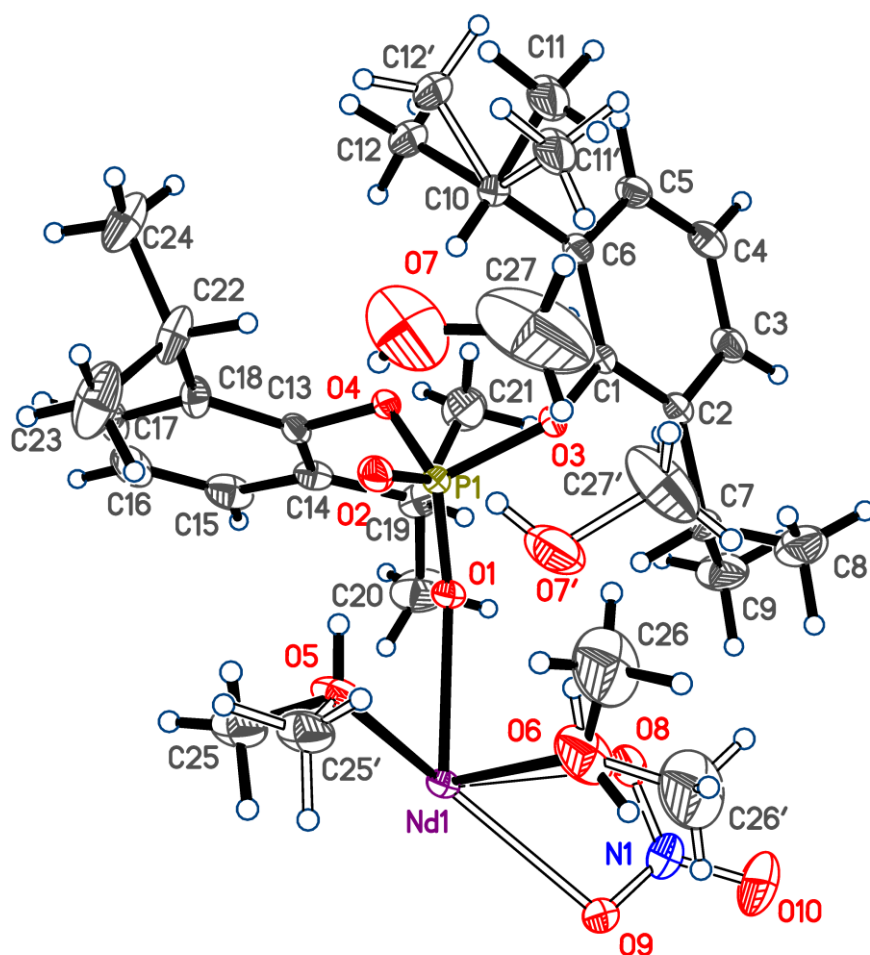


Figure S5 The asymmetric unit and disordered fragments in (4). Displacement ellipsoids for non-H atoms are drawn at 50% probability level. Occupancies of the Nd1, N1, O8, O9 and O10 atoms are 50%.

S2.3. Polyhedron assignment with the Hepta program

Fractional atomic coordinates within the unit cell were transformed into Cartesian coordinates for atoms O1, O1A, O5, O5A, O6, O6A, Cl1, Ln1 [Ln=Nd (1), Lu (2), Y (3)] with the Mercury program (into the xyz-file format). The xyz file was corrected to match the input format for the Hepta program.

Table S3 Calculation results for (1)-(3). Smallest deviations (dimensionless) from different geometries.

Cmpd.	Pentagonal bipyramid, D_{5h}	Capped octahedron, C_{3v}	Capped trigonal prism, C_{2v}	Capped octahedron (standard angles), C_{3v}	Capped trigonal prism (standard angles), C_{2v}
(1)	8.7908	15.0795	12.1925	14.9068	13.8391
(2)	6.5391	15.4040	12.8074	14.9307	13.6377
(3)	7.1521	15.3307	12.6003	14.9325	13.7653

S2.4. Comparison of some bond lengths

The differences between bond lengths and crystallographic rare-earth radii (Δ_{Ln-L} , Table S4) have been considered for the correct comparison of Ln – ligand bond distances. $\Delta_{Ln-L} = [d(Ln-L) - r(Ln)]$, where $d(Ln-L)$ is a metal-ligand bond distance, $r(Ln)$ is an ionic radius for the corresponding coordination number [for $CN_{Ln}=7$: $r(Nd)=1.185$ Å for (1), $r(Lu)=1.058$ Å for (2), $r(Y)=1.101$ Å for (3); for $CN_{Nd}=8$: $r(Nd)=1.249$ Å for (4); see (Shannon, 1976; Raymond & Eigenbrot, 1980)]. We have found rather small deviations of the calculated differences Δ_{Ln-L} from averaged ones for the same bonds for compounds (1)-(3). All Δ_{Ln-O5} and Δ_{Ln-O6} values are virtually the same for (1)-(3). However, differences between Δ_{Ln-O1} and Δ_{Ln-O6} (or Δ_{Ln-O5}) are *ca.* 11% higher, being about the same in each compound, which clearly shows different covalent and ionic contributions into Ln – O bonding. All Δ_{Nd-L} values for (4) are 4% smaller than corresponding averaged Δ_{Ln-L} values for (1)-(3), resulting from the replacement of Cl^- with NO_3^- .

Table S4 The differences between ligand to metal bond distances and rare-earth radii, Δ_{Ln-L} (Å), and their maximal deviations (%) from averaged Δ_{Ln-L} for (1)-(3).

$\Delta_{Ln-L} = [d(Ln-L) - r(Ln)]$; $r(Ln)$ are taken for corresponding CN_{Ln} ($CN_{Ln}=7$ for (1)-(3) and $CN_{Nd}=8$ for (4)).

Bonds, Ln-L	Δ_{Nd-L} in (1)	Δ_{Lu-L} in (2)	Δ_{Y-L} in (3)	Averaged Δ_{Ln-L} for (1)- (3)	Maximal deviations for (1)-(3)	Δ_{Nd-L} in (4)
Ln – Cl1	1.502	1.524	1.519	1.515	0.6	-
Ln – O1	1.153	1.143	1.140	1.145	0.7	1.103
Ln – O5	1.302	1.273	1.277	1.284	1.4	1.234
Ln – O6	1.281	1.292	1.283	1.285	0.5	1.238