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ARTICLE

Insights into Crystal Packing of Phosphorylporphyrins Based on Topology of Intermolecular Interaction Energies

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To the memory of Dr. Oleg Shishkin, our friend and colleague, for all inspiration he had continuously provided.

Four metal complexes of 5,15-bis(diethoxyphosphoryl)-10,20-diphenylporphyrin **1M** (M = Cd(II), Ni(II), Pd(II), Pt(II)) were synthesized and crystallographically characterized. Crystal organization patterns were analyzed using DFT (B97-D3/def2-SVP) calculations of intermolecular interaction energies between complexes in the crystals. For the systematic analysis of crystal packing, the calculations were extended to previously reported compounds **1M** (M = H₂, Cu(II), Zn(II)). Quantitative analysis of the interaction energies shows the essential role of weak intermolecular interactions such as C-H...O, C-H...π and M...π in the formation of the basic structural motifs and their organization within the crystals. Interplay between axial coordination and weak intermolecular interactions provides the basis for rationalization of observed polymorphism and crystals isomorphism in this series of porphyrin complexes.

Introduction

The deliberate synthesis of crystalline framework solids based on molecular building blocks connected by metal centers or nodes is motivated by prospects of elaboration of materials with useful properties for a wide range of practical applications such as gas storage,^{1,2} molecular separations,³ sensing,⁴ drug delivery,^{5,6} molecular recognition, fabrication of nanoscale reactors and catalysis.⁷ While semi-empirical synthesis of such crystalline solids based on careful selected building blocks represents a rapidly developing field of material science,⁸ an *a priori* prediction of crystal structures, being still in its infancy⁹ implies this field as one of the priorities for the development of modern crystallography. It should be noted that successful prediction of the crystal structure requires understanding of the crystal organization from an energetic viewpoint.¹⁰

Although the computational chemistry methods are recognized as valuable tool for analysis of intermolecular interactions in crystals,¹¹ these methods are often used as supplementary to classic contact-based approach to analysis of crystal packing. However, in many cases, such as absence of strong specific intermolecular interactions, determination of main forces in the crystal packing and supramolecular packing

motifs without use of computational methods could be very problematic.^{12–18} It should be noted, that in such cases consideration of the full map of intermolecular interactions is important, in order to correctly assign all main interactions and determine the role of secondary interactions. A suitable approach for analysis of topology of intermolecular interactions in molecular crystals was suggested recently.^{19–21} It is based on investigation of energies and directionality of pairwise interactions between basic molecule (BM) located in asymmetric part of unit cell and its closest neighbors forming the first coordination sphere of BM. Application of this approach allows to determine unambiguously a basic structural motif (BSM) of the crystal as an infinite fragment of the crystal containing all the most strongly bonded molecules. Moreover, analysis of various crystal structures based on topology of intermolecular interactions provides quite simple and reliable classification of types of organization of molecular crystals and impact of different intermolecular interactions in the crystals.²²

This approach was applied previously for molecular crystals containing only organic molecules, such as derivatives of phenanthroline,²³ benzene,²⁴ fluorinated pyridines²⁵ etc., but never for coordination compounds. There is a principal difference between the molecular interactions in the crystal for

these two series. In the crystal formed by organic compounds, molecules are connected by relatively weak non-bonding interactions such as stacking interactions, hydrogen or halogen bonds. The metal centers in the coordination compounds induce additional intermolecular interactions that may influence on the calculation results (for example, additional coordination bonds of the metal centers with donor atoms of adjacent molecules). To demonstrate the validity of a developed computation approach for the description of coordination compounds, 5,10-bis(diethoxyphosphoryl)porphyrins **1M** (Chart 1) seems to be a suitable series. Indeed, the crystal structure of free base porphyrin **1H₂** is known and represents a conventional starting point for the analysis. Moreover, it was shown that crystal packing of the complexes **1M** is determined by intermolecular interactions of different types. An axial coordination by the metal centers of one porphyrinate molecule with the oxygen atoms of phosphoryl groups of adjacent molecules may afford 2D coordination polymers in Zn(II) and Cu(II) porphyrinates **1Zn**²⁶ and **1Cu**²⁷. For **1Cu** another polymorph was found, in which Cu(II) ion does not form any additional axial coordination bonds and the crystal is stabilized by general electrostatic and dispersion interactions between large tetrapyrrolic macrocycles as well as hydrogen bonds formed due to interaction of the substituent with the macrocycle, i.e., C-H...O. The *ab initio* calculations should allow comparison of the impact of different molecular interactions on the crystal packing.

It should be noted that computational insight into the self-assembling of porphyrins is of particular interest because this process is widely observed in natural processes and extensively studied using synthetic models such as carboxylate and pyridine substituted porphyrins to prepare functional materials.^{28–32} In the most cases self-assembling of porphyrins in the crystals is viewed assuming the formation of coordination or/and hydrogen bonds as the strongest interactions between molecules to determine the crystal packing. However, taking into account relatively large size of the porphyrin moiety and the asymmetric geometry of the macrocyclic core it is possible to assume that the energy of non-bonding interactions between two porphyrinate molecules in the crystal may be comparable with the energy of the formation of weak coordination bonds. Therefore, type of self-assembling of porphyrins in the crystals may be considerably different from the viewpoint of energy of intermolecular interactions as compared to a conventional geometrical approach based on interatomic distances. In order to analyze this possibility it is necessary to consider crystal structure based on values of intermolecular interaction energies.

With this in mind, this article reports structural and computational analyses of transition metal complexes of 5,15-bis(diethoxyphosphoryl)-10,20-diphenylporphyrin **1H₂**³³ (Chart 1). Cadmium(II), nickel(II), palladium(II) and platinum(II) complexes **1Cd**, **1Ni**, **1Pd** and **1Pt** were synthesized and characterized by means of X-ray analysis in order to complete the literature data on the crystal packing of Zn(II) and Cu(II) derivatives. Moreover, the description of all structurally characterized complexes in terms of their energy and

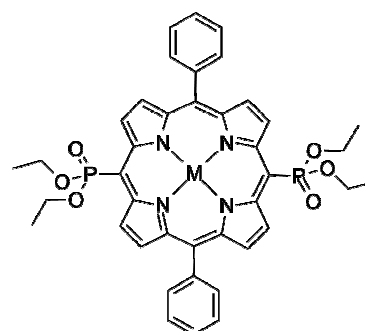


Chart 1. The structure of 5,15-bis(diethoxyphosphoryl)-10,20-diphenylporphyrin and metal complexes **1M**, M=H₂ (**1H₂**, chloroform solvate); M=Cd(II) (**1Cd**, 2D polymer); M=Zn(II), (**1Zn**, 2D polymer); M=Cu(II) (**1Cu(a)**, dioxane adduct; **1Cu(b)**, 2D polymer; **1Cu(c)** polymorph formed by discrete molecules); M=Ni (**1Ni**, hexane solvate); M=Pd (**1Pd**); M=Pt (**1Pt**).

directionality instead of a traditional geometrical approach based on interatomic distances was performed. According to this approach, all crystal structures may be divided into two types with different supramolecular architectures of the crystals and a prediction of new polymorphs and crystal packing for other metal complexes seems to be possible.

Experimental section

Synthesis of metal porphyrinates **1M** (M=Cd, Pt, Pd, Ni)

5,15-Bis(diethoxyphosphoryl)-10,20-diphenylporphyrin **1H₂** was obtained according to the Hiraio reaction.²⁶ Reaction of **1H₂** with aqueous cadmium acetate in the presence of sodium hydrocarbonate in a CHCl₃/MeOH mixture at room temperature afforded complex **1Cd** in 96% yield. Palladium complex **1Pd** was prepared in quantitative yield reacting **1H₂** with palladium acetate for 10 min in a CHCl₃/MeOH mixture at reflux. The reaction of **1H₂** with platinum chloride proceeded in benzonitrile at reflux affording complex **1Pt** in lower yield (77%). For the synthesis of the nickel complex in quantitative yield, nickel(II) acetate or acetylacetonate were reacted with **1H₂** in 1,2-dichlorobenzene at reflux. Synthetic details, as well as NMR, IR and mass spectra characterization of the complexes are provided as ESI.[‡]

X-ray diffraction study

Single crystals of **1Cd**, **1Ni**, **1Pd** and **1Pt** were obtained by slow evaporation of 3·10⁻³ mol/L chloroform/hexane solutions. Single-crystal X-ray diffraction experiments were carried out on a Bruker SMART APEX II diffractometer with a CCD area detector (graphite monochromator, Mo-K α radiation, λ = 0.71073 Å, ω -scans). The semi-empirical method SADABS³⁴ was applied for the absorption correction. The structures were solved by direct methods and refined by the full-matrix least-squares technique against F² with the anisotropic displacement parameters for all non-hydrogen atoms. All the hydrogen atoms in the complexes were placed geometrically and included in the structure factors calculation in the riding motion approximation.

Table 1 Crystal and experimental data for **1Cd**, **1Ni**, **1Pd** and **1Pt**.

	1Cd	1Ni	1Pd	1Pt
Mol. formula	C ₄₀ H ₃₈ N ₄ O ₆ P ₂ Cd	2[C ₄₀ H ₃₈ N ₄ O ₆ P ₂ Ni]·C ₆ H ₁₄	C ₄₀ H ₃₈ N ₄ O ₆ P ₂ Pd	C ₄₀ H ₃₈ N ₄ O ₆ P ₂ Pt
<i>M</i>	845.08	1668.96	839.08	927.77
Crystal system	monoclinic	triclinic	monoclinic	monoclinic
Space group	P2 ₁ /c	P-1	C2/c	P2 ₁ /c
<i>a</i> / Å	12.4567(16)	13.151(5)	16.128(4)	12.0856(13)
<i>b</i> / Å	11.7829(15)	13.187(5)	18.158(5)	13.6274(15)
<i>c</i> / Å	12.1147(16)	13.280(5)	13.503(3)	11.4059(13)
<i>α</i> / °	90	91.426(6)	90	90
<i>β</i> / °	91.889(2)	110.824(5)	113.570(3)	91.489(2)
<i>γ</i> / °	90	107.172(5)	90	90
<i>V</i> / Å ³	1777.2(4)	2034.8(13)	3624.3(16)	1877.9(4)
<i>Z</i>	2	1	4	2
<i>D</i> _{calc}	1.579	1.362	1.538	1.641
<i>μ</i> (mm ⁻¹)	0.760	0.608	0.655	3.874
<i>T</i> / K	153	150	296	296
No. of reflns	18896	17371	9482	16131
No. of unique reflns	4664	7866	4750	4907
No. of reflns with <i>I</i> > 2σ(<i>I</i>)	3675	5094	3072	3507
<i>R</i> _{int}	0.059	0.053	0.055	0.032
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)]	0.033	0.083	0.044	0.023
w <i>R</i> ₂ [all data]	0.081	0.256	0.095	0.065
CCDC number	998790	998788	998789	998787

All the data reduction and further calculations were performed using the OLEX2³⁵ and SHELX 2013³⁶ program packages. Selected crystal of **1Ni** was a non-merohedral twin with component ratio 0.637(4):0.443(4), twin matrix: [-0.821, 0.030, -0.911; 0, -1, 0; -0.357, -0.060, 0.821]. CCDC 998787-998790 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk. Crystallographic details are given in Table 1, detailed discussion of molecular structures of the complexes are provided as ESI.

Methods of calculations

The analysis of supramolecular architecture of the studied structures was performed using an approach based on calculation of pairwise interaction energies between molecules in crystal.^{20,21} First coordination sphere of each molecule in asymmetric part of unit cell was determined separately as it was suggested before.³⁷ The analysis of the topology of intermolecular interactions in the crystal is based on vector properties of intermolecular interactions.²¹ According to this approach, intermolecular interaction between two molecules in the crystal may be described by vector originated in the geometrical center of one molecule and directed toward the geometrical center of a second molecule. Length of this vector is calculated using the following equation:

$$L_i = (R_i E_i) / 2E_{\text{str}}$$

where *R_i* is the distance between the geometrical centers of interacting molecules, *E_i* is the energy of interaction between these two molecules and *E_{str}* is the energy of the strongest pairwise interaction in the crystal.

Application of this approach makes possible to construct the energy-vector diagram or “hedgehog” of intermolecular interactions reflecting the spatial distribution of intermolecular interactions of the basic molecule with the molecules belonging to its first coordination sphere. This diagram or hedgehog represents an image of the molecule in terms of intermolecular interactions in the crystal and it may be multiplied by all symmetry operations of the crystal structure giving a general picture of the topology of intermolecular interactions in the crystal. The strongest intermolecular interactions are represented by direct lines connecting geometrical centers of the most strongly bonded molecules.

Interaction energies for dimers were calculated using B97-D3/Def2-SVP density functional method³⁸⁻⁴² and corrected for basis set superposition error by counterpoise method.⁴³ The B97-D3 functional was benchmarked to be one of the most powerful dispersion-corrected density functional for calculations of intermolecular interactions.⁴⁴ It was also demonstrated that dispersion-corrected density functionals are very robust for calculations of bond energies with transition metals.^{45,46} DFT calculations were performed with ORCA 3.0 software.⁴⁷ Molecular geometry of dimers were taken from crystal, positions of hydrogen atoms were normalized to 1.089 Å for C-H and 1.015 Å for N-H bonds.

Results and discussion

To understand the influence of metal centers on the crystal organization of the studied complexes, it is important to consider the crystal structure of the free ligand **1H₂**. In the crystal phase porphyrin **1H₂** exists as CHCl₃ disolvate (Figure 1a).³³ Previously, based on geometrical analysis of intermolecular contacts only weak C-H...O intermolecular hydrogen bonds between solvate chloroform molecule and

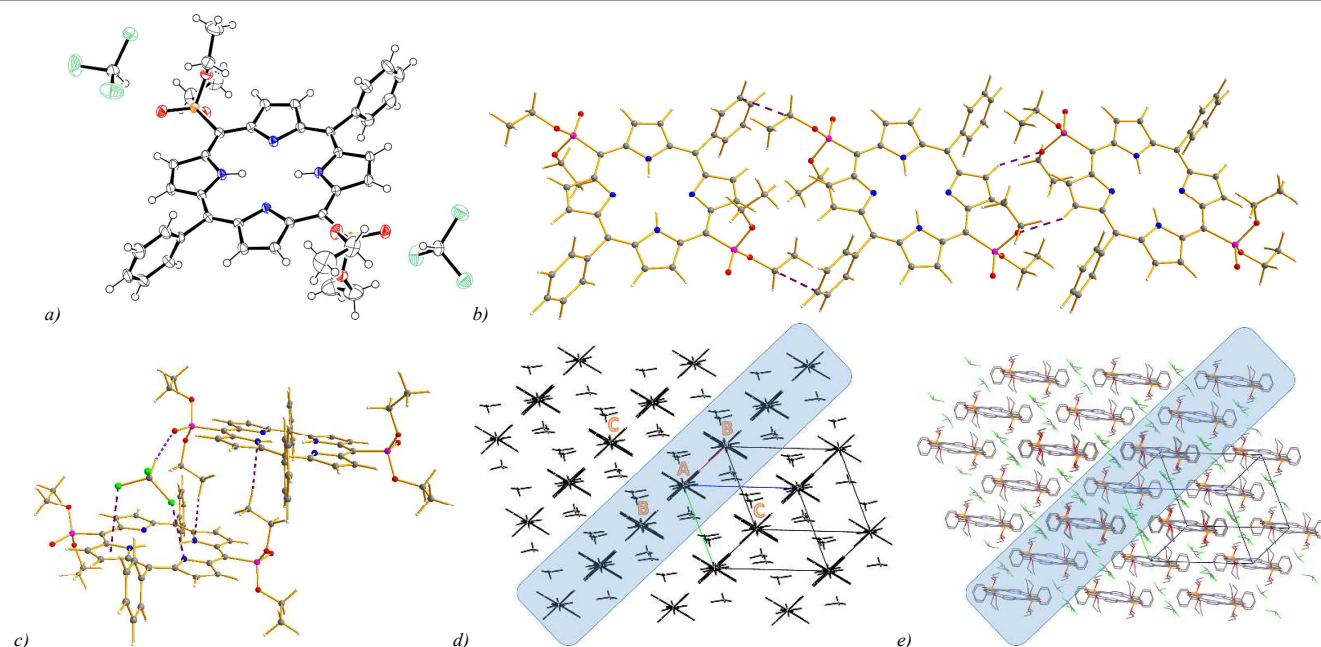


Fig. 1 Molecular structure of **1H₂** with displacement ellipsoids at 50% probability level (a), chains of strongly interacting molecules composed of dimers **1H₂-d1** and **1H₂-d2** (b), and interactions of **CHCl₃** with two porphyrin molecules, dimers **1H₂-d8** and **1H₂-d10** (c). Packing of energy vector diagrams (d) and molecular packing (e) of **1H₂** (view along the [2 1 -1] crystallographic direction). Chains of molecules **1H₂** are labeled as A-C, the basic structural motif of the crystal is highlighted.

phosphoryl oxygen atom of porphyrin were found. Therefore, definition of the basic structural motif of the crystal was a very complicated task.

In contrast, the results of calculations according to the energetic approach demonstrate that the supramolecular architecture of the crystal may be easily rationalized based on analysis of topology of intermolecular interactions. The highest

intermolecular interaction energies are observed in two centrosymmetric dimers **1H₂-d1** and **1H₂-d2** with a similar geometry (Table 2, Figure 1b). These dimers link molecules into infinite chains along the [2 1 -1] crystallographic direction. In these chains, mean planes of porphyrin rings of neighboring molecules are parallel and distances between them (d_{pl}) are less than 1.5 Å. This means that interactions between porphyrin

Table 2. The strongest intermolecular interactions in the crystal structures of **1H₂** and **1Cu(a)**.

Dimer	Symmetry operation	E_{int} , kcal/mol	Linked molecules ^a	d_{pl} / d_{displ} , Å	Contacts
1H₂-d1	-x,-y,2-z	-16.6	P...P	1.37 / 12.10	2x C-H...O 2x C-H...π
1H₂-d2	2-x,1-y,1-z	-13.6	P...P	1.47 / 13.12	2x C-H...π
1H₂-d3	1+x,y,z -1+x,y,z	-12.4	P...P	5.23 / 9.71	2x C-H...π
1H₂-d4	1-x,-y,2-z	-10.9	P...P	6.60 / 6.41	2x C-H...π
1H₂-d5	1-x,-y,1-z	-10.0	P...P	4.65 / 10.84	4x C-H...O
1H₂-d6	1-x,1-y,2-z	-9.8	P...P	4.75 / 10.53	-
1H₂-d7	1-x,1-y,1-z	-9.3	P...P	6.69 / 7.03	2x C-H...π
1H₂-d8	x,y,z	-8.9	P...S1	-	C-H...O
1H₂-d9	x,y,z	-8.4	P...S2	-	C-H...O
1H₂-d10	1-x,1-y,1-z	-7.9	P...S1	-	Cl...N
1H₂-d11	1-x,-y,2-z	-6.9	P...S2	-	Cl...N
1Cu(a)-d1	1+x,y,-1+z -1+x,y,1+z	-15.9	P...P	1.70 / 12.58	2x C-H...O 2x C-H...π
1Cu(a)-d2	x,y,z	-12.4	P...S	-	Cu...O
1Cu(a)-d3	-x,-y,-z x,y,1+z x,y,-1+z	-11.1	P...P	4.83 / 13.89	2x C-H...π
1Cu(a)-d4	x,1+y,z	-10.5	P...P	5.22 / 10.00	2x C-H...π
1Cu(a)-d5	x,-1+y,z 1+x,y,z -1+x,y,z	-10.5	P...P	6.52 / 7.12	4x C-H...O

^a P, S correspond to porphyrin and solvent molecules, respectively

molecules occur within the equatorial plane. Chains are stabilized by several intermolecular C-H...O (H...O 2.49 Å, C-H...O 149°) and C-H... π (H...C 2.87-2.95 Å, C-H...C 158-135°) hydrogen bonds between phosphoryl and phenyl groups. Large number of such weak interactions leads to noticeable overall interaction energy of a basic molecule with its two neighbors within the same chain, of about -30 kcal/mol.

Molecules of each chain formed by porphyrin **1H₂** interact with molecules of four neighboring chains (chains B and C on Figure 1d). Interactions between chains are also provided by multiple weak C-H...O (H...O 2.62-2.72 Å, C-H...O 142-157°) and C-H... π (H...C 2.66-3.03 Å, C-H...C 141-159°) hydrogen bonds between phosphoryl and phenyl groups.

The total interaction energies of a basic molecule (BM) belonging to chain A with molecules from chains B and C are -22.5 and -16.6 kcal/mol, respectively. The values of the energy ratio (ER) between total energies of interaction of BM to molecules within the same chain and from each of the neighboring chains are 1.3 and 1.8 that indicate some anisotropy of interaction energies between the chains. Thus, chain A together with the two neighboring chains B form a layer (Figure 1e) which is parallel to the (0 1 1) crystallographic plane. This layer may be considered as the secondary BSM of the crystal, if only porphyrin molecules are taken into account. Energy of interactions of BM to molecules of neighboring chains within the same BSM is by 2.7 times higher than the energy of interaction to molecules belonging to the neighboring layer.

Moreover, the results of calculation indicate that interactions of porphyrin and CHCl₃ molecules are rather strong and cannot be neglected for definition of BSM. Indeed, the chloroform molecules are located between the layers (Figure 1c). Each CHCl₃ molecule is in a contact with two porphyrin molecules belonging to neighboring chains of the same layer due to the formation of the C-H...O hydrogen bonds. The total energies of interactions of each chloroform molecule to one layer of porphyrins is considerably higher ($E_{\text{int}} = -18.5$ and -19.2 kcal/mol for two symmetrical independent CHCl₃ molecules) than to molecules **1H₂** from neighboring layer ($E_{\text{int}} = -5.9$ and -4.9 kcal/mol). The solvent molecules make significant contribution into formation of layered structure in

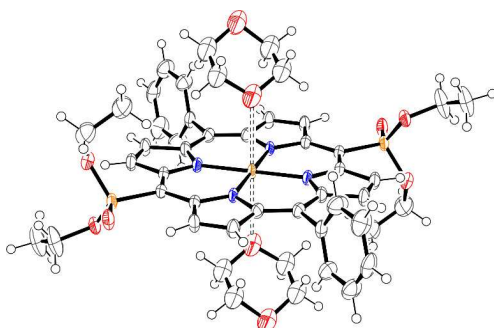


Fig. 2 Molecular structure of **1Cu(a)** with displacement ellipsoids at 50% probability level.

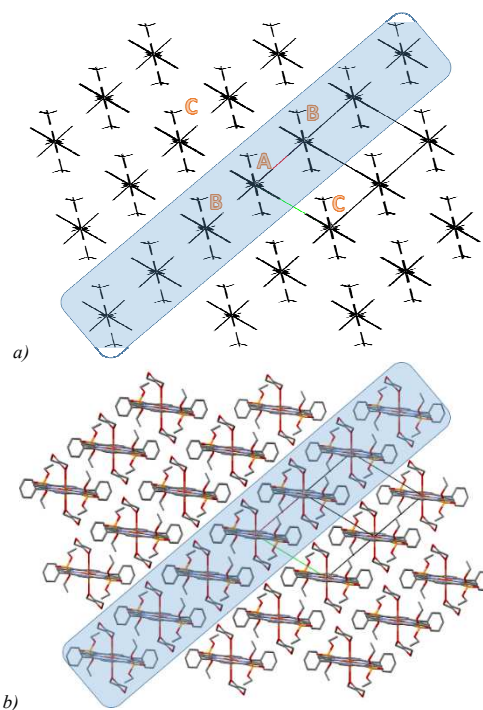


Fig. 3 Packing of energy vector diagram (a) and molecular packing (b) of **1Cu(a)** (view along the [1 0 1] crystallographic direction). Chains of complexes are labelled as A-C, basic structural motif of the crystal is highlighted.

the **1H₂** crystal and should be considered as a part of BSM.

Computational analysis of the crystal structure of **1Cu(a)**²⁷ reveals substantial similarity with **1H₂**. In **1Cu(a)** the Cu(II) ion is located at the center of the macrocyclic ring (Cu...N 2.01-2.02 Å) and forms weak coordination bonds in axial directions with the oxygen atoms of two dioxane molecules with Cu...O 2.73 Å (Figure 2). For analysis of the topology of intermolecular interactions Cu-porphyrin and dioxane molecules were considered as separate molecules taking into account the long Cu...O distance.

Results of calculations demonstrate that the most strongly bonded dimers are formed by two molecules of **1Cu(a)** complex (Table 2). It is interesting to note that their geometry is very similar to that of the most strongly bonded dimer in the crystal **1H₂**. This may be seen from the values of $d_{\text{pl}}/d_{\text{displ}}$ and specific interactions summarized in Table 2. The intermolecular interactions in the dimer **1Cu(a)**-d1 are similar to those observed for dimers **1H₂**-d1 and **1H₂**-d2. In both crystals, these dimers are stabilized by weak C-H...O and C-H... π hydrogen bonds between phosphoryl and phenyl groups. Interaction energies of corresponding dimers in two structures are also very close. This results in the same BSM in both crystals. In **1Cu(a)** molecules are linked in chains along the [0 1 1] crystallographic direction. Interaction energy of BM with two neighbors within the chain is -31.8 kcal/mol, while the interaction energies with complexes from neighboring chains B and C (Figure 3) are -21.6 and -17.7 kcal/mol (ER=1.5 and 1.8, respectively). Hence, in **1Cu(a)** chains are organized in layers along the (0 1 0) crystallographic plane with ER value being 2.4.

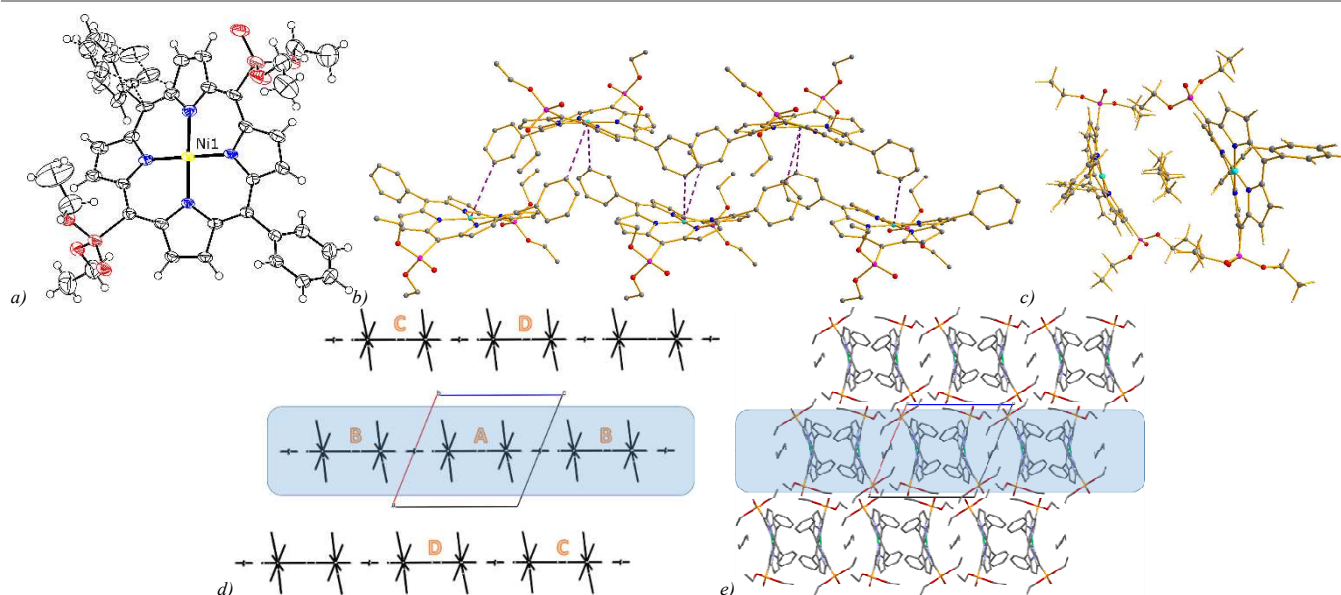


Fig. 4 Molecular structure of **1Ni** with displacement ellipsoids at 50% probability level (a), strongly interacting chains composed of dimers **1Ni-d1** and **1Ni-d2** (b), and interactions of hexane with two porphyrin molecules, dimers **1Ni-d5** (c) and packing of energy vector diagrams (d) and molecular packing (e) of **1Ni** (view along the [0 1 0] crystallographic direction). Chains of strongly interacting complexes labeled as A-D, basic structural motif of the crystal is highlighted.

The dioxane molecules in **1Cu(a)** are located by two sides of a porphyrin ring in similar positions as observed for chloroform molecules in **1H₂**. In contrast to the structure of **1H₂**, each solvent molecule is strongly bonded to only one complex **1Cu(a)** as indicated by the energy of the two porphyrinate...dioxane interactions which are equal to -12.4 kcal/mol and -5.1 kcal/mol. Thus, the solvent molecules stabilize layers as BSM of the crystal.

Therefore, the crystals **1H₂** and **1Cu(a)** are very similar both from a viewpoint of crystal organization as well as the topology of intermolecular interactions despite of differences in geometrical parameters and unit cell dimensions (Table S1). It could be supposed that formation of dioxane adduct with unusual bipyramidal coordinated copper(II) is supported by weak intermolecular interactions which form remarkably stable BSM of the crystal.

The role of the solvent molecules in the crystal organization is even more prominent for **1Ni**. The crystal contains Ni-porphyrin complexes (Figure 4a) and solvent hexane molecule according the ratio 2:1. Ni(II) ion resides within the porphyrin cavity and defines a nearly perfect square-planar coordination

with Ni-N distances of 1.89-1.91 Å, porphyrin macrocycle has four-saddle conformation with pyrrole rings being twisted with respect to the mean plane of the N-atoms of porphyrin by 21.2-23.3°. In contrast to **1Cu(a)** complex, the Ni(II) ion is not involved into additional axial coordination. Instead, in the crystal each porphyrin macrocycle is surrounded by two phenyl rings belonging to two neighboring molecules (dimers **1Ni-d1** and **1Ni-d2** in Table 3). These phenyl substituents form the C-H... π hydrogen bonds with BM (H...N 2.36-2.61 Å, C-H...N 136-149°). It should be noted that one of the phenyl rings is disordered over the two positions *I* and *II* with an occupancy ratio 0.657(4):0.443(4) which differ by the rotation of the phenyl ring by about 50°. This leads to somewhat different interaction energies for the two disordered positions in dimers **1Ni-d1** and **1Ni-d2**. The energy of interactions of each complex with two neighbors within the chain is -60.4 and -57.3 kcal/mol for the two positions of disordered phenyl substituent. The most strongly bonded **1Ni-d1** and **1Ni-d2** dimers link porphyrin complexes into zig-zag chains (Figure 4b) along the [0 1 0] crystallographic direction. Each chain in the crystal is surrounded by six neighboring chains, three of which are

Table 3. The strongest intermolecular interactions in the crystal structure of **1Ni**.

Dimer	Symm. operation	E_{ints} , kcal/mol		Linked molecules ^a	$d_{\text{pt}} / d_{\text{displ}}$, Å	Contacts
		I^b	II^b			
1Ni-d1	-x,2-y,-z	-23.1	-23.6	P...P	5.94 / 7.26	4x C-H... π
1Ni-d2	-x,1-y,-z	-18.2	-19.4	P...P	5.90 / 6.25	4x C-H... π
1Ni-d3	1-x,2-y,1-z	-12.8	-12.8	P...P	1.27 / 11.96	2x C-H...O
1Ni-d4	-1-x,1-y,-z	-12.2	-14.0	P...P	0.1 / 12.55	2x C-H...O
1Ni-d5	x,y,z	-11.6	-11.6	P...H	-	-
	-x,2-y,1-z					

^a P and H correspond to porphyrin and hexane molecules, respectively

^b *I* and *II* correspond for two disordered positions of the phenyl ring

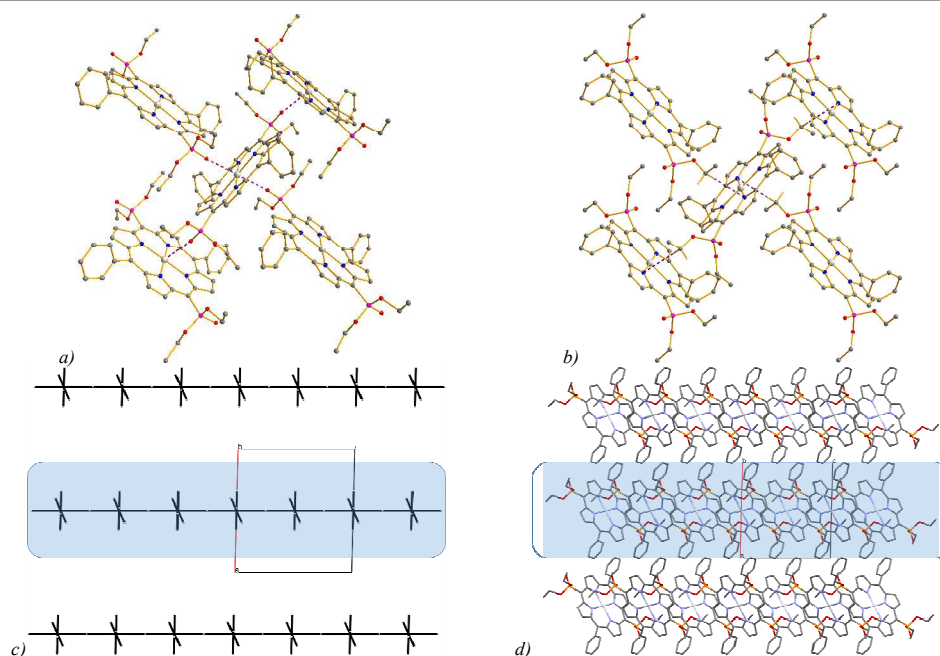


Fig. 5 Structure of 2D in **1Cd**, **1Cu(b)** and **1Zn** formed due to axial M...O=P coordination bonds (a) and CH... π interactions in **1Pt** (b) (to note the different orientation of the diethoxyphosphoryl group). Packing of energy vector diagrams of **1Cu(b)**, **1Zn**, **1Cd** and **1Pt** (c) and corresponding molecular packing (d) (view along the [1 0 0] crystallographic directions). Basic structural motif of the crystal is highlighted.

symmetrically non-equivalent (Figure 4d). Interaction energies of the **1Ni-d1** dimer from chain A containing BM with complexes from chains B, C and D are -21.3, -24.1 and -27.4 kcal/mol for disordered position *I* and -21.2, -24.1 and -29.0 kcal/mol for position *II*, respectively.

At the same time, chains A and B are additionally bound due to interactions with hexane molecules, which are located inside a cavities formed by two distorted macrocycles (Figure 4c). The interaction energy of hexane with each of two porphyrin complexes in such trimer is rather high (-11.6 kcal/mol). Thus, solvent molecules link neighboring zig-zag chains A and B into infinite layer along the (0 1 1) crystallographic plane which should be considered as the BSM of the crystal. Therefore, it is possible to conclude that

supramolecular architecture of the crystals of free ligand **1H₂** and its complexes with copper and nickel have the same type of layered supramolecular architecture. In all structures, the BSM is a layer stabilized by solvent molecules.

The crystal organization of **1Cd**, **1Cu(b)**²⁷, **1Zn**²⁶ and **1Pt** is significantly different from that of the complexes discussed above (Figure 5). These crystals are isostructural (Tables 1 and S1), the complexes occupy a special position and the metal atom is located on an inversion center. In **1Cu(b)**, **1Zn** and **1Cd** metal ions form additional axial coordination bonds with two phosphoryl oxygen atoms of neighboring molecules leading to the formation of 2D coordination polymer (Figure 5). The M-O distances (Cu...O 2.65 Å, Cd...O 2.63 Å and Zn...O 2.46 Å) allow assigning 4+2 coordination number to the metal

Table 4. The strongest intermolecular interactions in the crystal structures of **1Cu**, **1Zn**, **1Cd** and **1Pt**.

Dimer	Symmetry operation	E_{int} , kcal/mol						
		1Cu(b)		1Zn		1Cd	1Pt	
		<i>I</i> ^a	<i>II</i> ^a	<i>I</i> ^a	<i>II</i> ^a		<i>I</i> ^a	<i>II</i> ^a
d1	1-x,1/2+y,1/2-z 1-x,1/2+y,3/2-z 1-x,-1/2+y,1/2-z 1-x,-1/2+y,3/2-z	-25.2	-26.2	-30.1	-29.5	-30.9	-23.8	-22.6
d2	-x,1/2+y,1/2-z -x,-1/2+y,1/2-z 2-x,1/2+y,3/2-z 2-x,-1/2+y,3/2-z	-6.6	-6.7	-6.4	-4.2	-6.5	-5.2	-5.0
d3	x,y,1+z x,y,-1+z	-6.6 ^b		-4.8	-4.2	-5.5	-11.7	-11.4
d4	1+x,y,z -1+x,y,z	-6.0	-6.0	-6.0	-5.9	-5.9	-7.8	-7.8

^a *I* and *II* correspond for two disordered positions of ethyl group

center.

Analysis of the calculated interaction energies demonstrates that the d1 dimer in **1Cu(b)**, **1Zn** and **1Cd** containing axial coordination bonds possesses the highest intermolecular interaction energy (Table 4). Interaction energy in **1Cu(b)** is noticeably lower, than in **1Zn** and **1Cd**, reflecting a lower propensity of Cu(II) for formal octahedral or square-bipyramidal coordination in porphyrin complexes. Except of the M...O interactions, the most strongly bonded dimer d1 of **1Cu(b)**, **1Zn** and **1Cd** is also stabilized by several intermolecular C-H... π bonds between H-atoms and π -systems of two almost orthogonal pyrrole rings (H...N 2.52-2.63 Å, C-H...N 143-148° and H...C 2.91-2.92 Å, C-H...C 124-127°). These interactions could be considered to be very similar to the C-H... π bonds observed in **1Ni-d1** and **1Ni-d2**.

The four most strongly bonded dimers in the crystals of **1Cu(b)**, **1Zn**, **1Cd** determine a layer along the (0 0 1) crystallographic plane (Figure 5) which should be considered as BSM of the crystals. Energy of interaction of the BM with neighbors within the same layer (-118.2 – -139.6 kcal/mol) is 5.3-7.4 times higher than the energy of interaction of the BM with molecules belonging to a neighboring layer (-21.2 – -22.5 kcal/mol).

The **1Pt** complex is of particular interest. Platinum(II) atom always lies in a square-planar environment and cannot form additional coordination bonds by axial coordination of donor atoms. However, this crystal has the same layered supramolecular architecture as **1Cu(b)**, **1Zn** and **1Cd**. In this structure the P=O bond is rotated by about 180°, compared to **1Cu(b)**, **1Zn** and **1Cd** (Figure 5b). Therefore, the ethyl groups

Table 5. The strongest intermolecular interactions in the crystal structures of **1Cu(c)** and **1Pd**.

Dimer	Symm. operation	E_{int} , kcal/mol	Contacts
1Cu(c)-d1	-x,1-y,1-z	-51.4	2x Cu... π 6x C-H...O 2x C-H... π
	-x,1-y,2-z		
1Cu(c)-d2	1/2-x,1/2-y,2-z	-15.0	2x C-H...O
	-1/2-x,1/2-y,1-z		
1Cu(c)-d3	x,y,1+z	-4.3	-
	x,y,-1+z		
1Pd-d1	-x,y,1/2-z	-24.6	2x C-H... π
1Pd-d2	1-x,y,3/2-z	-16.1	2x C-H...O 2x C-H... π
	1/2+x,1/2+y,z		
1Pd-d3	-1/2+x,-1/2+y,z	-9.3	2x C-H...O
	1/2+x,-1/2+y,z		
1Pd-d4	-1/2+x,1/2+y,z	-7.9	-
	-x,y,3/2-z		
	1-x,y,1/2-z		

are oriented towards the ring of adjacent porphyrin molecule. This leads to the formation of multiple weak C-H... π hydrogen bonds (H...C 2.85-2.98 Å, C-H...C 125-153°). Results of calculations demonstrate that the most strongly bonded dimer d1 in **1Pt** has a structure which is rather similar to other isostructural complexes. The intermolecular interaction energy in d1 of **1Pt** is surprisingly close to those observed in **1Cu(b)**, **1Zn** and **1Cd** (Table 4). The four most strongly bonded dimers determine a layer along the (0 0 1) crystallographic plane as the BSM of the crystal with almost the same ER of 5.9-6.1 as for other isostructural crystals. However, in **1Pt** the BSM is stabilized by multiple weak C-H... π hydrogen bonds instead of the M-O coordination bonds. These data demonstrate that weak

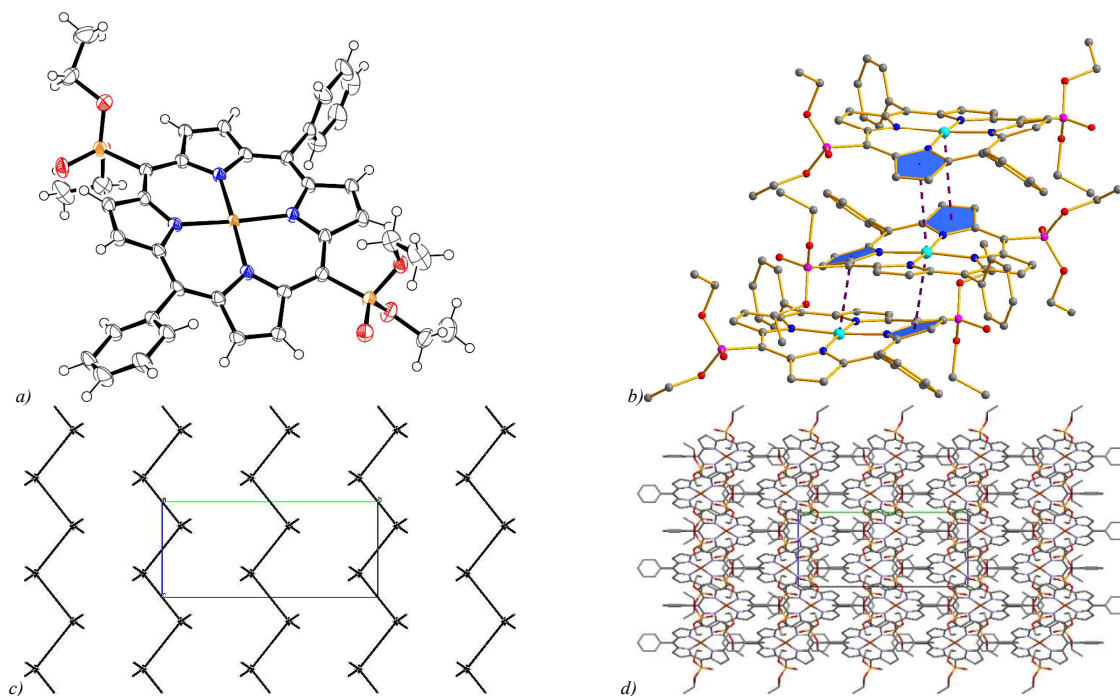


Fig. 6 Molecular structure of **1Cu(c)** with displacement ellipsoids at 50% probability level (a) and chain of strongly interacting molecules composed of dimers **1Cu(c)-d1** (b). Packing of energy vector diagrams of **1Cu(c)** (c) and corresponding molecular packing (d) (view along the [1 0 0] crystallographic directions).

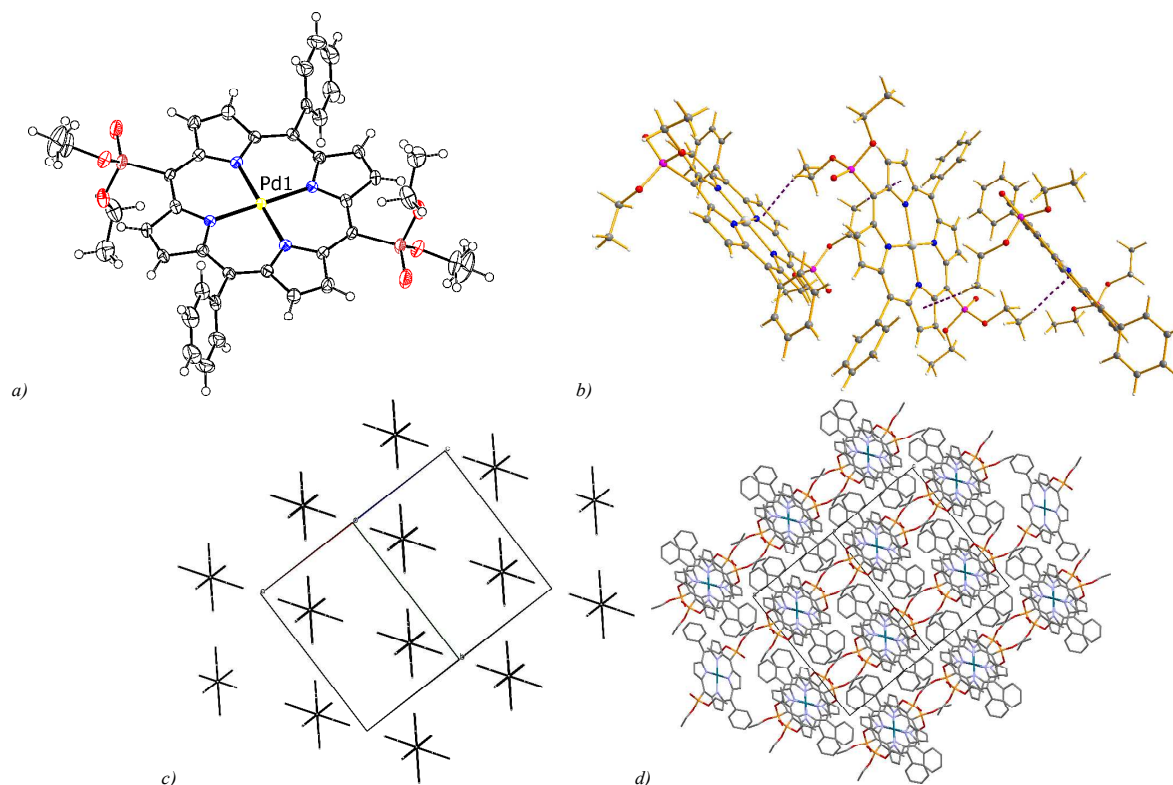


Fig. 7 Molecular structure of **1Pd** with displacement ellipsoids at 50% probability level (a), columns of strongly interacting complexes (b). Packing of energy vector diagrams (c) and corresponding molecular packing (d) (view along the [1 0 1] crystallographic direction).

intermolecular interactions may be as important as weak coordination bond for the crystal organization.

This conclusion is also supported by analysis of the supramolecular architecture of the **1Cu(c)**²⁷ crystal, which is a second polymorph of **1Cu(b)** (Figure 6). In this polymorph, the metal atom does not form any additional coordination bonds to heteroatoms and the tetrapyrrolic macrocycle is non-planar. The crystal organization differs from those of **1Cu(b)** and **1Pt**. In axial directions the Cu(II) atoms have close contacts with C_β atoms of pyrroles rings of neighboring molecules with a distance Cu...C of 3.13 Å. These contacts could be attributed to Cu...π interactions which stabilize the most strongly bonded dimers in the crystal **1Cu(c)** (labelled as **1Cu(c)-d1** in Table 5). These dimers link complexes into columns along the [0 0 1] crystallographic direction (Figure 6b). In the columns, complexes are also linked by multiple weak intermolecular C-H...O hydrogen bonds (H...O 2.40-2.68 Å, C-H...O 137-138°). Calculated interaction energies of a BM with two neighbors within the column and molecules belonging to neighboring columns is -102.7 kcal/mol and -22.3 kcal/mol respectively (ER=4.6). It should be noted that the packing of columns is isotropic from a viewpoint of intermolecular interaction energies. Thus, the columns represent the BSM of this crystal (Figure 6c-d).

To better rationalize the origin of the difference of BSM in the crystals of planar porphyrinate **1Pt** and non-planar **1Cu(c)**, it is of interest to compare the crystal packing of these

compounds to that of **1Pd**, which is a structural analog of **1Pt** at the molecular level (Figure 7a).

In **1Pd** crystal, the metal is located on an inversion center within a nearly perfectly planar porphyrin macrocycle with Pd-N distances of 2.019(2) Å. Diethoxyphosphoryl groups of two neighboring complexes are located above and below the Pd(II) ion, and ethyl groups are oriented towards the metal as in **1Pt**. As a result only the C-H...π intermolecular hydrogen bonds (H...C 2.71 Å, C-H...C 158°) are formed in the most strongly bonded dimer of **1Pd-d1** (Table 5). Surprisingly, supramolecular architecture of the **1Pd** does not resemble the structure of **1Pt**, but rather the **1Cu(c)** structure. The most strongly bonded dimers determine the columns along the [1 0 1] crystallographic direction (Figure 7b). Energy of interaction of BM with two neighbors within the column is -49.3 kcal/mol⁻¹. Six neighboring columns (Figure 7c-d) surround each column, but the strongest interactions (-20.4 kcal/mol, ER=2.4) are observed with only four columns. Isotropically packed columns thus represent the BSM of **1Pd**, similarly to **1Cu(c)**.

It should be noted that despite similarity of coordination properties of Pt(II) and Pd(II), these crystals show a different supramolecular architectures. Taking into account similar values of interaction energies in the most strongly bound dimers defining BSM of **1Pt** and **1Pd** crystals, it is possible to suggest the existence of a second polymorph for each complex.

Conclusions

The above results demonstrate that the analysis of topology of intermolecular interactions is crucial for a rational description of crystal packing of porphyrins and their metal complexes. Weak intermolecular interactions, even those which are not usually regarded by the traditional contact-based analysis for the crystal packing oftentimes play an important role in supramolecular organization. Similar conclusions were made, for example, for low-melting complexes of small oxygen-containing molecules with haloforms,³⁷ substituted bicyclic aziridines,²⁰ and even for fused hydrocarbons.²¹

Analysis of the supramolecular architecture of the crystals of the phosphorylporphyrin **1H₂** and its complexes with transition metals reveals the existence of two types of crystal structures where infinite layers or columns represent the basic structural motif (BSM) of the crystal. Character of BSM depends on the constituents of the crystal and the nature of interactions between molecules. Layered architecture is observed for the crystal containing solvent molecules or additional coordination bonds between porphyrines. Absence of additional coordination of metal or solvent results in the formation of columnar crystal structures where molecules within columns are bonded by multiple weak intermolecular interactions (structures **1Cu(c)** and **1Pd**). The platinum(II) complex represents an exception from this general trend. Layers in this crystals are formed without participation of solvent molecules and stabilized by numerous weak C-H... π bonds between the porphyrin molecules.

It should be noted the similarity of supramolecular architecture of the crystals of free ligand **1H₂** and its complexes with copper and nickel containing different solvate molecules. This allows to suggest that non-bonding interactions between large porphyrin molecules is a competitive factor influencing self-assembling in the solid state together with the influence of metal centers and solvent molecules. The same conclusion may be made for **1Cu(b)**, **1Zn**, **1Cd** and **1Pt** complexes. Despite the differences in metal coordination environment, they are isostructural and have very similar crystal organization from energetic viewpoint.

Importance of weak non-bonded interactions in the organization of the crystals is also evidenced by the existence of two polymorphs of **1Cu** complex with. One of them has layered structure stabilized by the Cu...O additional coordination bonds while the BSM of the second polymorph is a column, formed by multiple weak non-bonded interactions. This allows to assume the possibility of the formation of at least one additional polymorph for the crystals of other complexes. Indirect confirmation of this suggestion is also provided by comparison of the crystal structures of **1Pt** and **1Pd** complexes. They have similar molecular structure and character of intermolecular interactions but a different supramolecular architecture.

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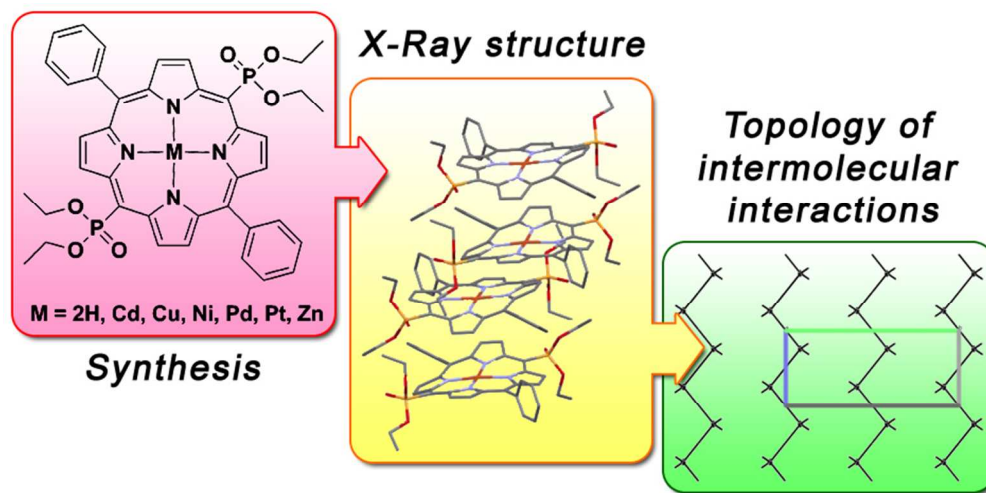
[†] Passed away 17 July 2014

[‡] Electronic Supplementary Information (ESI) available: synthesis, characterization, ¹H and ³¹P NMR spectra for **1Cd**, **1Pd**, **1Pt** and **1Ni**, details on molecular structure for the complexes, unit cell dimensions and crystal symmetry for **1H₂**, **1Cu(a)**, **1Cu(b)**, **1Cu(c)** and **1Zn**, complete list of intermolecular interaction energies in the crystals. See DOI: 10.1039/b000000x/

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Crystal structure of the series of phosphorylporphyrin complexes was analysed in terms of intermolecular interaction energies.

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