

Supporting Information

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

Roman I. Zubatyuk,^{a*} Anna A. Sinelshchikova,^b Yulia Y. Enakieva,^b Yulia G. Gorbunova,^{bc} Aslan Y. Tsivadze,^{bc} Sergey E. Nefedov,^c Alla Bessmertnykh-Lemeune,^d Roger Guillard,^b Oleg V. Shishkin^{ae*}

^a SSI “Institute for Single Crystals” National Academy of Science of Ukraine, Kharkiv 61001, Ukraine.

^b A.N. Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Leninsky Pr. 31, Moscow, 119071, Russia.

^c N.S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Leninsky Pr. 31, Moscow, 119991, Russia.

^d Université de Bourgogne, ICMUB (UMR CNRS 6302), 9 Avenue Alain Savary, BP 47870, 21078 Dijon Cedex, France.

^e V.N. Karazin Kharkiv National University, Kharkiv 61202, Ukraine.

E-mail: roman@xray.isc.kharkov.com

Synthesis and characterization of 1Cd, 1Pd, 1Pt and 1Ni.

Unless otherwise noted, all chemicals and starting materials were obtained commercially from Acros and Sigma-Aldrich Co. and used without further purification. 5,15-bis(diethoxyphosphoryl)-10,20-diphenylporphyrin (**1H₂**) was synthesized according to the literature procedure (Y. Y. Enakieva, A. G. Bessmertnykh, Y. G. Gorbunova, C. Stern, Y. Rousselin, A. Y. Tsivadze, and R. Guillard, *Org. Lett.*, 2009, **11**, 3842). All reactions were performed in oven-dried glassware under a slight positive pressure of argon. Chloroform and methanol were freshly distilled before use. Silica gel 60 (0.063–0.20 mm, 70–230 mesh ASTM, Merck) and aluminum oxide (0.063–0.20 mm, basic, activated Brockmann II-III, Merck) was used for column chromatography. Analytical thin-layer chromatography (TLC) was carried out using Merck silica gel 60 plates (precoated sheets, 0.2 mm thick, with fluorescence indicator F254).

¹H and ³¹P NMR spectra were recorded at 300 MHz on a Bruker Avance 300 III NanoBay. All chemical shifts are given in ppm, referenced on the δ scale using residual solvent peak as internal standard for ¹H, and phosphoric acid (H₃PO₄) as external standard for ³¹P NMR. Coupling constants are given in Hz. UV-visible spectra were recorded on a Varian Cary 100 spectrophotometer. Mass spectra were obtained in linear mode with a Bruker Proflex III MALDI-TOF mass spectrometer without matrix and accurate mass measurements (HRMS) using a Orbitrap ESI-TOF mass spectrometer. IR spectra were registered on a FT-IR Nexus (Nicolet) spectrometer using micro-ATR accessory (Pike). HRMS and FT-IR measurements were made at the "Pôle Chimie Moléculaire", the technological platform for chemical analysis and molecular synthesis (<http://www.wpcm.fr>) which relies on the Institute of the Molecular Chemistry of University of Burgundy and Welience™, a Burgundy University private subsidiary.

CADMIUM(II) 5,15-BIS(DIETHOXYPHOSPHORYL)-10,20-DIPHENYLPORPHYRINATE (1Cd). A solution of porphyrin **1H₂** (15.6 mg, 2.12·10⁻² mmol), cadmium acetate (19.6 mg, 8.50·10⁻² mmol) and NaHCO₃ (28.2 mg, 0.336 mmol) in chloroform - methanol mixture (2.85 ml, 9/1 v/v) was stirred at room temperature for 1.5 h. The volatiles were removed in vacuo. A green residue was purified by column chromatography on basic alumina using a mixture CHCl₃/MeOH (99/1% v/v) as eluent. Complex **1Cd** was obtained as a green solid (17.2 mg, 96%). ¹H NMR (300 MHz, CDCl₃/CD₃OD, 2/1 v/v, 25 °C): δ 1.17 (t, *J* = 7.0, 12H, CH₃), 4.07-3.97 (m, 4H, CH₂O), 4.33 – 4.20 (m, 4H, CH₂O), 7.59 (m, 6H, *m*-,*p*-Ph), 7.96 (d, *J* = 7.4, 4H, *o*-Ph), 8.56 (d, *J* = 4.7, 4H, β -

H), 9.88 (d, $J = 4.7$ Hz, 4H, β -H). ^{31}P NMR ($\text{CDCl}_3/\text{CD}_3\text{OD}$, 2/1 v/v, 121 MHz, 25 °C): δ 25.4 (s). FT-IR (ν_{max} , cm^{-1}): 2916(w), 2850(w), 1595(w), 1508(m), 1438(m), 1382(m), 1226(s), 1196(s), 1083(m), 1075(m), 1033(m), 983(m), 950(s), 885(s), 802(m), 754(m), 730(m), 700(m), 665(m). UV-Vis (CHCl_3 , λ_{max} , nm ($\lg(\epsilon)$): 430 (5.26), 572 (3.92), 610 (4.28). HRMS: m/z $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{40}\text{H}_{38}\text{N}_4\text{CdO}_6\text{P}_2\text{Na}$: 869.12035, found: 869.11603.

PALLADIUM(II) 5,15-BIS(DIETHOXYPHOSPHORYL)-10,20-DIPHENYLPORPHYRINATE (1Pd).

Palladium(II) acetate (14.4 mg, $6.41 \cdot 10^{-2}$ mmol) was added to a solution of **1H₂** (11.8 mg, $1.6 \cdot 10^{-2}$ mmol) in a mixture of CHCl_3 (3 ml) and CH_3OH (0.15 ml). The reaction mixture was stirred at reflux for 10 min. After cooling, the volatiles were evaporated under reduced pressure. A pink residue was dissolved in CHCl_3 and purified by column chromatography on silica gel using hexane/ CHCl_3 (40/60% v/v) as eluent. The product was obtained as a pink solid **1Pd** (13.0 mg, 97%). ^1H NMR (CDCl_3 , 300 MHz, 25 °C): δ 1.35 (t, $J = 7.0$, 12H, CH_3), 4.28 – 4.15 (m, 4H, CH_2O), 4.56 – 4.43 (m, 4H, CH_2O), 7.83 – 7.73 (m, 6H, m -, p -Ph), 8.11 (d, $J = 7.0$, 4H, o -Ph), 8.86 (d, $J = 5.2$, 4H, β -H), 10.32 (d, $J = 5.2$, 4H, β -H). ^{31}P NMR (CDCl_3 , 121 MHz, 25 °C): δ 21.0 (s). FT-IR (ν_{max} , cm^{-1}): 2975(w), 2926(w), 1600(w), 1543(m), 1431(m), 1390(m), 1348(m), 1251(s), 1203(m), 1151(w), 1092(m), 1000(m), 950(s), 883(s), 802(s), 750(s), 702(s), 665(m). UV-Vis (CHCl_3 , λ_{max} , nm, $\lg(\epsilon)$): 412(5.54), 538(4.28), 577(4.77). HRMS: m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{40}\text{H}_{39}\text{N}_4\text{PdO}_6\text{P}_2$: 839.13889, found: 839.13525; $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{40}\text{H}_{38}\text{N}_4\text{PdO}_6\text{P}_2\text{Na}$: 861.12083, found: 861.11766.

PLATINUM(II) 5,15-BIS(DIETHOXYPHOSPHORYL)-10,20-DIPHENYLPORPHYRINATE (1Pt).

Platinum(II) chloride (18 mg, $6.76 \cdot 10^{-2}$ mmol) was added to a solution of porphyrin **1H₂** (25 mg, $3.40 \cdot 10^{-2}$ mmol) in benzonitrile (6 ml). The reaction mixture was stirred at reflux for 3 h. The volatiles were removed in vacuo. A pink residue was purified by column chromatography on silica gel using gradient elution of a hexane/ CHCl_3 mixture. The fraction eluted using 75/25% v/v mixture of hexane/ CHCl_3 gave after an evaporation of the solvents platinum(II) 5-mono(diethoxyphosphoryl)-10,20-diphenylporphyrinate (**2Pt**) (4.3 mg, 16%). The fraction eluted using 70/30% v/v mixture of hexane/ CHCl_3 afforded complex **1Pt** after evaporation of the solvents. Complex **1Pt** was obtained as a pink solid (24.4 mg, 77%).

1Pt. ^1H NMR (CDCl_3 , 300 MHz, 25 °C): δ 1.36 (t, $J = 7.0$, 12H, CH_3), 4.26 – 4.19 (m, 4H, CH_2O), 4.53-4.47 (m, 4H, CH_2O), 7.76 (t, $J = 7.3$, 4H, p -Ph), 7.82 (t, $J = 7.1$, 2H, m -Ph), 8.11 (d, $J = 6.9$, 4H; o -Ph), 8.83 (d, $J = 5.2$, 4H, β -H), 10.29 (d, $J = 5.2$ Hz, 4H, β -H). ^{31}P NMR

(CDCl₃, 121 MHz, 25 °C): δ 20.5 (s). FT-IR (ν_{\max} , cm⁻¹): 2925(w), 2854(w), 1600(w), 1530(w), 1440(m), 1390(w), 1354(m), 1253(s), 1160(m), 1085(m), 1005(vs), 945(vs), 884(s), 801(m), 750(s), 703(m), 665(m). UV-Vis (CHCl₃, λ_{\max} , nm (lg(ϵ)): 401 (5,21), 532 (3,97), 569 (4,42). HRMS: m/z [M+H]⁺ calcd for C₄₀H₃₉N₄PtO₆P₂: 928.19904, found: 928.19544; [M+Na]⁺ calcd for C₄₀H₃₈N₄PtO₆P₂Na: 950.17761, found: 950.18098.

2Pt. ¹H NMR (CDCl₃, 300 MHz, 25 °C): δ 1.34 (t, J = 7.1, 6H, CH₃), 4.30 – 4.17 (m, 2H, CH₂O), 4.56 – 4.43 (m, 2H, CH₂O), 7.79 (m, 6H, *m*-,*p*-Ph), 8.15 (d, J = 7.4, 4H, *o*-Ph), 8.85 (d, J = 4.9, 2H, β -H), 8.90 (d, J = 5.5, 2H, β -H), 9.17 (d, J = 4.9, 2H, β -H), 10.12 (s, 1H, *meso*-H), 10.37 (d, J = 5.4, 2H, β -H), ³¹P NMR (CDCl₃, 121 MHz, 25 °C): δ 21.76 (s). UV-Vis (CHCl₃, λ_{\max} , nm (lg(ϵ)): 396 (5,12), 510 (4,13), 548(4,25). MS (MALDI-TOF): m/z [M]⁺ calcd for C₃₆H₂₉N₄PtO₃P: 791.16, found 791.561.

NICKEL(II) 5,15-BIS(DIETHOXYPHOSPHORYL)-10,20-DIPHENYLPORPHYRINATE (1Ni). **Method A.** Porphyrin **1H₂** (10.0 mg, 1.36·10⁻² mmol) and nickel(II) acetylacetonate (14.0 mg, 5.45·10⁻² mmol) were dissolved in 2.5 ml of 1,2-dichlorobenzene. The reaction mixture was stirred at reflux for 5 min. After cooling, the reaction mixture was evaporated in vacuo. The violet residue was dissolved in CHCl₃ and purified by column chromatography on silica gel using hexane/CHCl₃ (15/85% v/v) as an eluent. Complex **1Ni** was isolated as a violet solid after evaporation of the solvents in vacuo (10.6 mg, yield 99%). **Method B.** Porphyrin **1H₂** (10.0 mg, 1.36·10⁻² mmol) and nickel(II) acetate (9.6 mg, 5.43·10⁻² mmol) were dissolved in 2 ml of 1,2-dichlorobenzene. The reaction mixture was stirred at reflux for 45 min. The solvent was removed under reduced pressure. The violet residue was dissolved in CHCl₃ and purified by column chromatography on silica gel using hexane/CHCl₃ (15/85% v/v). Compound **1Ni** was isolated as a violet solid after evaporation of the solvents in vacuo (9.3 mg, yield 87%). ¹H NMR (CDCl₃/CD₃OD, 2/1 v/v, 300 MHz, 25 °C): δ 1.14 (t, J = 7.1, 12H, CH₃), 4.03 – 3.87 (m, 4H, CH₂O), 4.16 – 4.07 (m, 4H, CH₂O), 7.50 (m, 6H, *m*-, *p*-Ph), 7.72 (d, J = 7.6, 4H, *o*-Ph), 8.52 (d, J = 5.1, 4H, β -H), 9.62 (d, J = 5.2, 4H, β -H). ³¹P NMR (CDCl₃/CD₃OD, 2/1 v/v, 121 MHz, 25 °C): δ 19.6 (s). FT-IR (ν_{\max} , cm⁻¹): 2980(w), 2900(w), 1600(w), 1535(m), 1436(m), 1390(m), 1348(m), 1253(s), 1203(m), 1158(m), 1092(m), 1013(s), 963(s), 888(s), 808(m), 750(s), 696(m), 663(m). UV-Vis (CHCl₃, λ_{\max} , nm, lg(ϵ)): 417(5.22), 553(3.92), 597(4.32). HRMS: m/z [M]⁺ calcd for C₄₀H₃₈N₄NiO₆P₂: 790.16146, found: 790.15959; [M+H]⁺ calcd for C₄₀H₃₉N₄NiO₆P₂: 791.16928, found: 791.16544; [M+Na]⁺ calcd for C₄₀H₃₈N₄NiO₆P₂Na: 813.15123, found: 813.14623.

Molecular structure of metal porphyrinates

Three of the studied complexes **1Cd**, **1Pd**, **1Pt** crystallized without solvent molecules while the crystal of **1Ni** contains solvate molecules of hexane. In all structures, the metal ion is a nearly perfect square-planar coordination defined by the four nitrogen atoms of the porphyrin macrocycle and the bond distance are determined by the nature of the metal ion. The shortest M–N bonds (1.885(6), 1.897(6), 1.909(6), 1.907(5) Å) are observed for electron-deficient nickel(II) complex in which the deviation of planar geometry of NiN₄ fragment did not exceed +/- 0.020 Å. Considerable non-planarity of the porphyrin ring is observed for **1Ni**. A four-saddle conformation of the macrocycle is observed with dihedral angles between mean planes of four N atoms and pyrrole rings of 21.2–22.3° (maximal deviations of C_β atoms from the N₄ plane are -0.690–0.570 Å). Such non-planarity is common for nickel porphyrinates and was also observed for **1Cu(c)**, however with much lower values of distortion angles i.e. 9.3–15.2°. In all structures, phosphoryl bond lies almost in the mean plane of porphyrin forming an intramolecular C–H...O hydrogen bond with C_β atom of the porphyrin. In non-planar **1Ni** complex, the phosphoryl groups are located significantly far away from the N₄ plane and situated out-side of the saddle porphyrinic scaffold at a distance of -1.287 Å and 1.342 Å. This geometry is reflected by the value of dihedral angles of the phosphoryl group CCC–O=P which are equal to 10.1° and 12.9°.

In **1Cd**, additional coordination bonds in axial direction are formed with phosphoryl group of the neighboring molecule, giving rise a of 2D polymeric structure (Cd–O distance is 2.6253(14) Å). The crystalline structure of this complex is similar to those of **1Cu(b)** and **1Zn**, already described by our groups.

It should be noted, that **1Pt** is isostructural to complexes **1Cd**, **1Cu(b)** and **1Zn** (Tables 1 and S1). However, the significant difference in the orientation of substituents with respect to the tetrapyrrolic macrocycle was observed for this compound compared to other complexes. In **1Pt** the phenyl ring is rotated by more than 80° with respect to the porphyrin plane, compared to 62–65° in the other structures. Moreover, even more prominent difference between these structures is the absence of axial coordination in **1Pt** and the orientation of the oxygen atom of phosphoryl group away from the metal center of an adjacent porphyrin molecule.

In all the discussed structures, except for porphyrin **1H₂** and its Ni(II) complex, molecules are located in a special position, metal ions lie on a two-fold axis (**1Cu(c)**) or on an inversion center (**1Cu(a)**, **1Cu(b)**, **1Cd**, **1Zn**, **1Pd**, **1Pt**).

Table S1 Unit cell dimensions and crystal symmetry for **1H2**, **1Cu(a)**, **1Cu(b)**, **1Cu(c)** and **1Zn**.

	1H₂	1Cu(a)	1Cu(b)	1Cu(c)	1Zn
formula	C ₄₀ H ₄₀ N ₄ O ₆ P ₂ , 2CHCl ₃	C ₄₀ H ₃₈ N ₄ O ₆ P ₂ Cu, 2C ₄ H ₈ O ₂	C ₄₀ H ₃₈ N ₄ O ₆ P ₂ Cu	C ₄₀ H ₃₈ N ₄ O ₆ P ₂ Cu	C ₄₀ H ₃₈ N ₄ O ₆ P ₂ Zn
<i>F_w</i>	973.44	972.43	796.22	796.22	798.05
crystal system	triclinic	triclinic	monoclinic	monoclinic	monoclinic
space group	P-1	P-1	P2 ₁ /c	C2/c	P2 ₁ /c
<i>a</i> [Å]	11.0237(7)	9.657(2)	12.3787(6)	19.565(6)	12.4813(4)
<i>b</i> [Å]	13.8769(9)	11.280(3)	11.7319(5)	20.676(7)	11.4995(4)
<i>c</i> [Å]	16.0768(11)	11.705(3)	12.2028(6)	9.063(3)	12.1377(5)
<i>α</i> [°]	77.8890(10)	71.456(4)	90	90	90
<i>β</i> [°]	70.4290(10)	72.223(4)	91.8580(10)	94.445(5)	91.668(2)
<i>γ</i> [°]	84.0270(10)	77.807(4)	90	90	90
<i>V</i> [Å ³]	2264.2(3)	1141.9(5)	1771.23(14)	3655(2)	1741.37(11)
<i>Z</i>	2	1	2	4	2

Table S2 Numbering of dimers, type of dimers, symmetry operation of second molecule of dimer and energy of intermolecular interactions (kcal/mol) in dimers formed by the basic molecule in the crystal **1H₂**. Dimers belonging to basic structural motif are highlighted in bold.

Dimer	Symmetry operation	Type ^a	E _{int}
1	x,y,z	P...C1	-8.9
2	x,y,z	P...C2	-8.4
3	x,y,1+z	P...C2	-2.6
4	x,y,-1+z	P...C1	-3.7
5	1+x,y,z	P...P	-12.4
6	1+x,y,z	P...C2	-0.9
7	1+x,y,-1+z	P...P	-6.7
8	1+x,y,-1+z	P...C1	-1.3
9	-1+x,y,z	P...P	-12.4
10	-1+x,y,z	P...C1	-1.1
11	-1+x,y,1+z	P...P	-6.7
12	-1+x,y,1+z	P...C2	-1.4
13	-x,-y,1-z	P...P	-2.0
14	-x,-y,2-z	P...P	-16.6
15	-x,-y,2-z	P...C1	-1.6
16	1-x,-y,1-z	P...P	-10.0
17	1-x,-y,2-z	P...P	-10.9
18	1-x,-y,2-z	P...C1	-6.9
19	1-x,1-y,1-z	P...C2	-7.9
20	1-x,1-y,1-z	P...P	-9.3
21	1-x,1-y,2-z	P...P	-9.8
22	2-x,1-y,1-z	P...C2	-2.0
23	2-x,1-y,1-z	P...P	-13.6
24	2-x,1-y,2-z	P...P	-1.8
25	x,y,z	C1...P	-8.9
26	x,y,1+z	C1...P	-3.7
27	x,y,1+z	C1...C2	-0.9
28	1+x,y,z	C1...P	-1.1
29	-1+x,y,1+z	C1...P	-1.3
30	-x,-y,2-z	C1...P	-1.6
31	1-x,-y,2-z	C1...P	-6.9
32	x,y,z	C2...P	-8.4
33	x,y,-1+z	C2...C1	-0.9
34	x,y,-1+z	C2...P	-2.6
35	1+x,y,-1+z	C2...P	-1.4
36	-1+x,y,z	C2...P	-0.9
37	1-x,1-y,1-z	C2...P	-7.9
38	2-x,1-y,1-z	C2...P	-2.0

^a P, C1 and C2 correspond to porphyrin and two symmetry unique chloroform molecules

Table S3 Numbering of dimers, type of dimers, symmetry operation of second molecule of dimer and energy of intermolecular interactions (kcal/mol) in dimers formed by the basic molecule in the crystal **1Cu(a)**. Dimers belonging to basic structural motif are highlighted in bold.

Dimer	Symmetry operation	Type ^a	Eint
1	x,y,z	P...D	-12.4
2	x,y,1+z	P...P	-11.1
3	x,y,-1+z	P...P	-11.1
4	x,y,-1+z	P...D	-1.3
5	x,1+y,z	P...P	-10.5
6	x,1+y,z	P...D	-3.8
7	x,1+y,1+z	P...P	-1.6
8	x,1+y,-1+z	P...D	-1.6
9	x,-1+y,z	P...P	-10.5
10	x,-1+y,-1+z	P...P	-1.6
11	1+x,y,z	P...P	-10.5
12	1+x,y,-1+z	P...P	-15.9
13	1+x,1+y,-1+z	P...P	-7.3
14	-1+x,y,z	P...P	-10.5
15	-1+x,y,z	P...D	-5.1
16	-1+x,y,1+z	P...P	-15.9
17	-1+x,y,1+z	P...D	-0.8
18	-1+x,-1+y,1+z	P...P	-7.3
19	-x,-y,-z	P...D	-12.4
20	-x,-y,1-z	P...D	-1.3
21	-x,-1-y,-z	P...D	-3.8
22	-x,-1-y,1-z	P...D	-1.6
23	1-x,-y,-z	P...D	-5.1
24	1-x,-y,-1-z	P...D	-0.8
25	x,y,z	P...P	-12.4
26	x,y,1+z	P...P	-1.3
27	x,-1+y,z	P...P	-3.8
28	x,-1+y,1+z	P...P	-1.6
29	1+x,y,z	P...P	-5.1
30	1+x,y,-1+z	P...P	-0.8
31	1-x,-1-y,-z	P...D	-2.3

^a P, and D correspond to porphyrin and dioxane molecules

Table S4 Numbering of dimers, type of dimers, symmetry operation of second molecule of dimer and energy of intermolecular interactions (kcal/mol) in dimers formed by the basic molecule in the crystal **1Ni**. Dimers belonging to basic structural motif are highlighted in bold.

Dimer	Symmetry operation	Type ^a	E _{int} ^b	
			A	B
1	x,y,z	P...H	-11.6	-11.6
2	x,1+y,z	P...P	-9.5	-7.1
3	x,-1+y,z	P...H	-2.2	-2.3
4	x,-1+y,z	P...P	-9.5	-7.1
5	1+x,y,z	P...P	-7.6	-7.5
6	1+x,y,z	P...H	-1.1	-1.1
7	1+x,y,1+z	P...P	-3.3	-3.4
8	-1+x,y,z	P...P	-7.6	-7.5
9	-1+x,y,-1+z	P...P	-3.3	-3.4
10	-x,1-y,-z	P...P	-18.2	-19.4
11	-x,1-y,1-z	P...P	-11.6	-11.5
12	-x,2-y,-z	P...P	-23.1	-23.6
13	-x,2-y,1-z	P...P	-9.7	-9.7
14	1-x,1-y,1-z	P...P	-4.6	-4.5
15	1-x,2-y,1-z	P...P	-12.8	-12.8
16	-1-x,1-y,-z	P...P	-12.2	-14.0
17	-1-x,2-y,-z	P...P	-2.6	-2.6
18	x,y,z	H...P	-11.6	-11.6
19	x,1+y,z	H...P	-2.2	-2.3
20	-1+x,y,z	H...P	-1.1	-1.1
21	-x,1-y,1-z	H...P	-2.2	-2.3
22	-x,2-y,1-z	H...P	-11.6	-11.6
23	1-x,2-y,1-z	H...P	-1.1	-1.1

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

^b For two disordered positions A and B of the porphyrin molecule

Table S5 Numbering of dimers, symmetry operation of second molecule of dimer and energy of intermolecular interactions (kcal/mol) in dimers formed by the basic molecule in the crystal **1Cu(c)**. Dimers belonging to basic structural motif are highlighted in bold.

Dimer	Symmetry operation	Eint
1	x,y,1+z	-4.3
2	x,y,-1+z	-4.3
3	x,1+y,z	-0.4
4	x,-1+y,z	-0.4
5	1/2+x,1/2+y,z	-3.4
6	1/2+x,1/2+y,1+z	-1.2
7	1/2+x,-1/2+y,z	-3.4
8	1/2+x,-1/2+y,1+z	-1.2
9	-1/2+x,1/2+y,z	-3.4
10	-1/2+x,1/2+y,-1+z	-1.2
11	-1/2+x,-1/2+y,z	-3.4
12	-1/2+x,-1/2+y,-1+z	-1.2
13	-x,-y,1-z	-1.4
14	-x,-y,2-z	-1.4
15	-x,1-y,1-z	-51.4
16	-x,1-y,2-z	-51.4
17	1/2-x,1/2-y,1-z	-1.4
18	1/2-x,1/2-y,2-z	-15.0
19	1/2-x,1/2-y,3-z	-1.3
20	-1/2-x,1/2-y,-z	-1.3
21	-1/2-x,1/2-y,1-z	-15.0
22	-1/2-x,1/2-y,2-z	-1.4

Table S6 Numbering of dimers, symmetry operation of second molecule of dimer and energy of intermolecular interactions (kcal/mol) in dimers formed by the basic molecule in the crystal **1Pd**. Dimers belonging to basic structural motif are highlighted in bold.

Dimer	Symmetry operation	Eint
1	1+x,y,z	-7.0
2	-1+x,y,z	-7.0
3	-x,y,1/2-z	-24.6
4	-x,y,3/2-z	-7.9
5	1-x,y,1/2-z	-7.9
6	1-x,y,3/2-z	-24.6
7	1/2+x,1/2+y,z	-16.1
8	1/2+x,-1/2+y,z	-9.3
9	-1/2+x,1/2+y,z	-9.3
10	-1/2+x,-1/2+y,z	-16.1
11	1/2-x,1/2+y,1/2-z	-7.7
12	1/2-x,1/2+y,3/2-z	-7.7
13	1/2-x,-1/2+y,1/2-z	-7.7
14	1/2-x,-1/2+y,3/2-z	-7.7

Table S7 Numbering of dimers, symmetry operation of second molecule of dimer and energy of intermolecular interactions (kcal/mol) in dimers formed by the basic molecule in the crystals **1Cu(b)**, **1Zn**, **1Cd** and **1Pt**. Dimers belonging to basic structural motif are highlighted in bold.

Dimer	Symmetry operation	Eint						
		1Cu(b)		1Zn		1Cd	1Pt	
		A	B	A	B		A	B
1	x,y,1+z	-6.6	-6.6	-4.8	-4.2	-5.5	-11.7	-11.4
2	x,y,-1+z	-6.6	-6.6	-4.8	-4.2	-5.5	-11.7	-11.4
3	x,1+y,z	-2.3	-2.1	-2.1	-3.2	-2.4	-0.7	-0.7
4	x,-1+y,z	-2.3	-2.1	-2.1	-3.2	-2.4	-0.7	-0.7
5	1+x,y,z	-6.0	-6.0	-6.0	-5.9	-5.9	-7.8	-7.8
6	1+x,1+y,z	-2.8	-2.8	-0.5	-0.6	-2.8	-1.1	-1.1
7	1+x,-1+y,1+z	-0.4	-0.5	-3.0	-2.9	-0.5	-0.3	-0.3
8	-1+x,y,z	-6.0	-6.0	-6.0	-5.9	-5.9	-7.8	-7.8
9	-1+x,1+y,-1+z	-0.4	-0.5	-3.0	-2.9	-0.5	-1.1	-1.1
10	-1+x,-1+y,z	-2.8	-2.8	-0.5	-0.6	-2.8	-0.3	-0.3
11	-x,1/2+y,1/2-z	-6.6	-6.7	-6.4	-4.2	-6.5	-5.2	-5.0
12	-x,-1/2+y,1/2-z	-6.6	-6.7	-6.4	-4.2	-6.5	-5.2	-5.0
13	1-x,1/2+y,1/2-z	-25.2	-26.2	-30.1	-29.5	-30.9	-23.8	-22.6
14	1-x,1/2+y,3/2-z	-25.2	-26.2	-30.1	-29.5	-30.9	-23.8	-22.6
15	1-x,-1/2+y,1/2-z	-25.2	-26.2	-30.1	-29.5	-30.9	-23.8	-22.6
16	1-x,-1/2+y,3/2-z	-25.2	-26.2	-30.1	-29.5	-30.9	-23.8	-22.6
17	2-x,1/2+y,3/2-z	-6.6	-6.7	-6.4	-4.2	-6.5	-5.2	-5.0
18	2-x,-1/2+y,3/2-z	-6.6	-6.7	-6.4	-4.2	-6.5	-5.2	-5.0

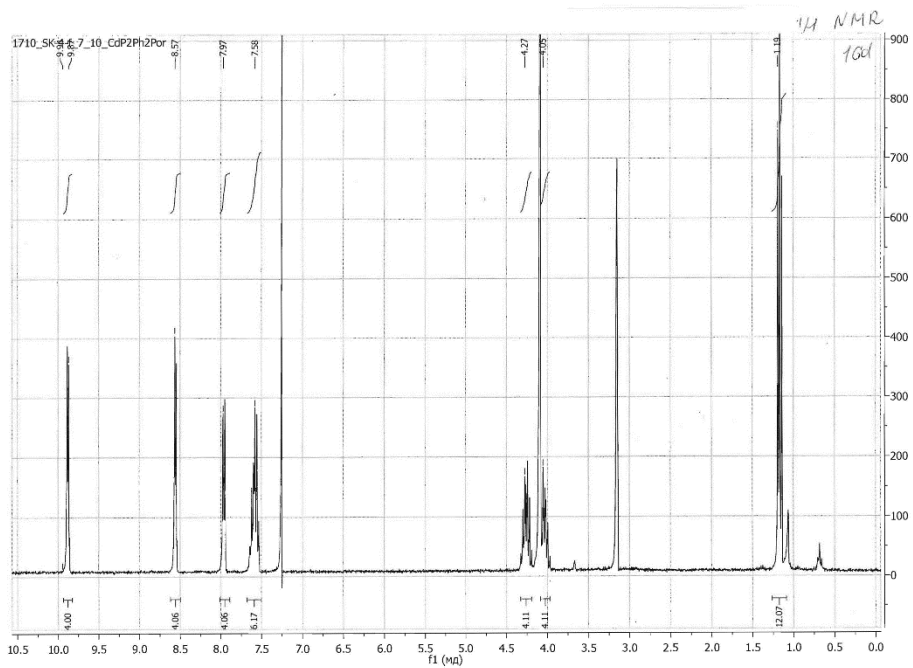


Fig S1 ^1H NMR for **1Cd** (300 MHz, $\text{CDCl}_3/\text{CD}_3\text{OD}$, 2/1 v/v, 25 °C)

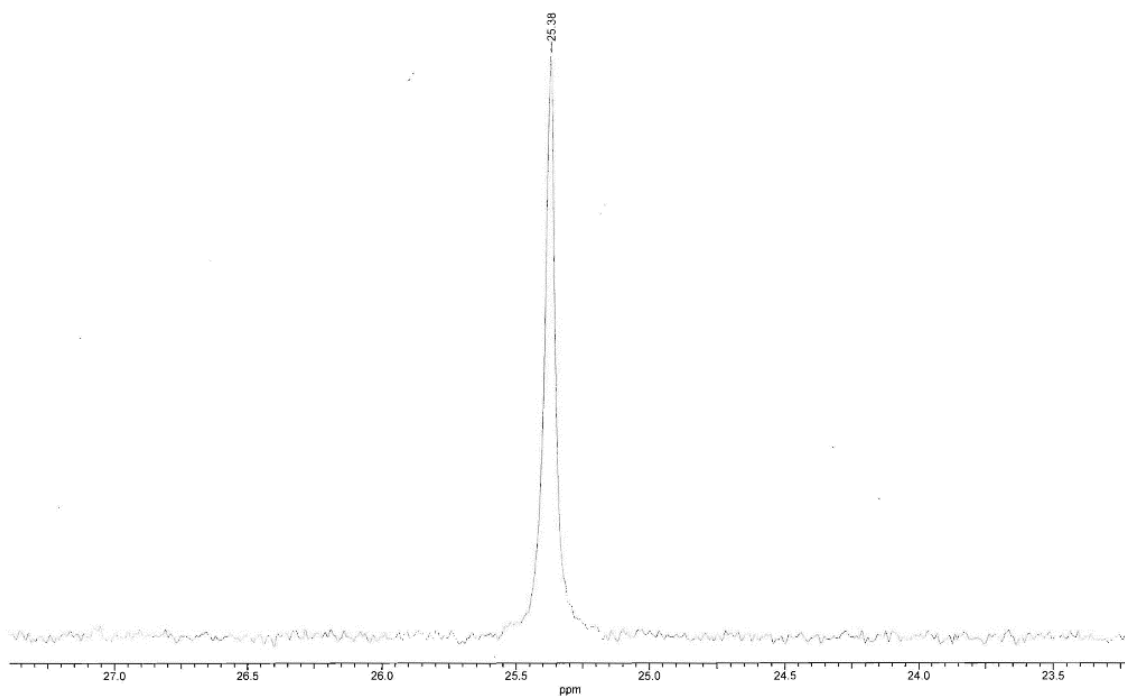


Fig S2 ^{31}P NMR for **1Cd** ($\text{CDCl}_3/\text{CD}_3\text{OD}$, 2/1 v/v, 121 MHz, 25 °C)

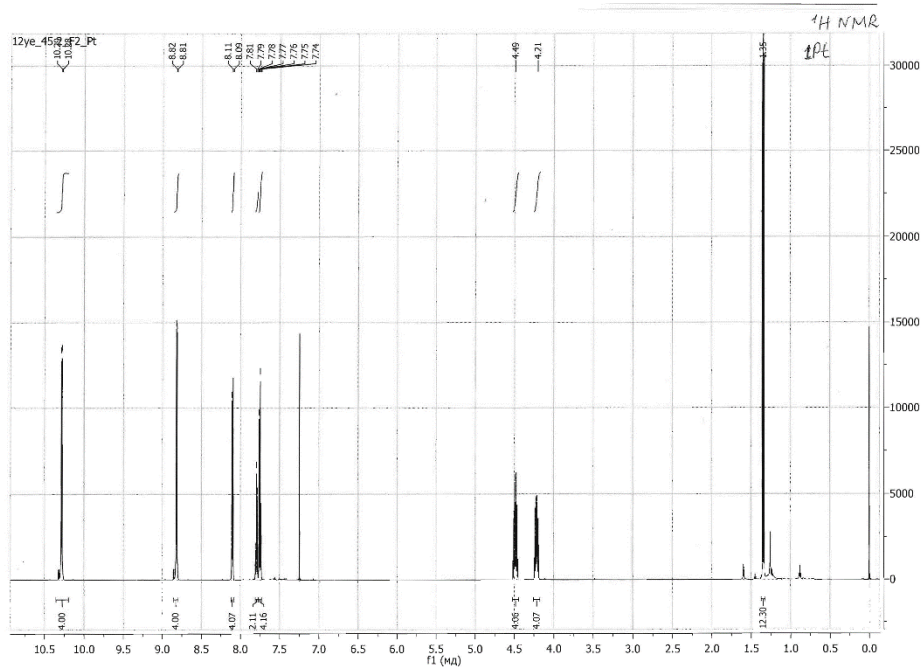


Fig S3 ^1H NMR for **1Pt** (CDCl_3 , 300 MHz, 25 °C)

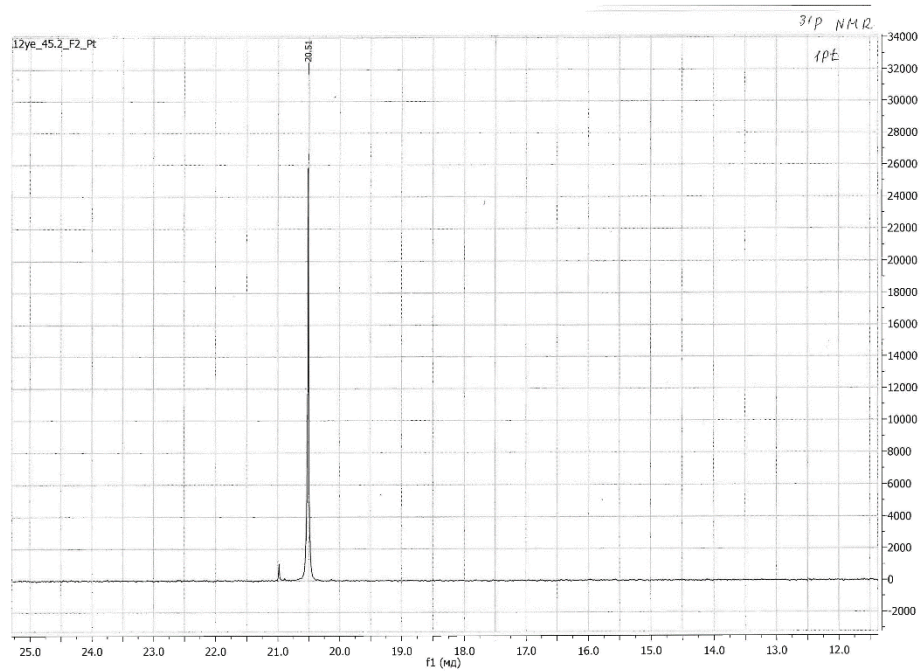


Fig S4 ^{31}P NMR for **1Pt** (CDCl_3 , 121 MHz, 25 °C)

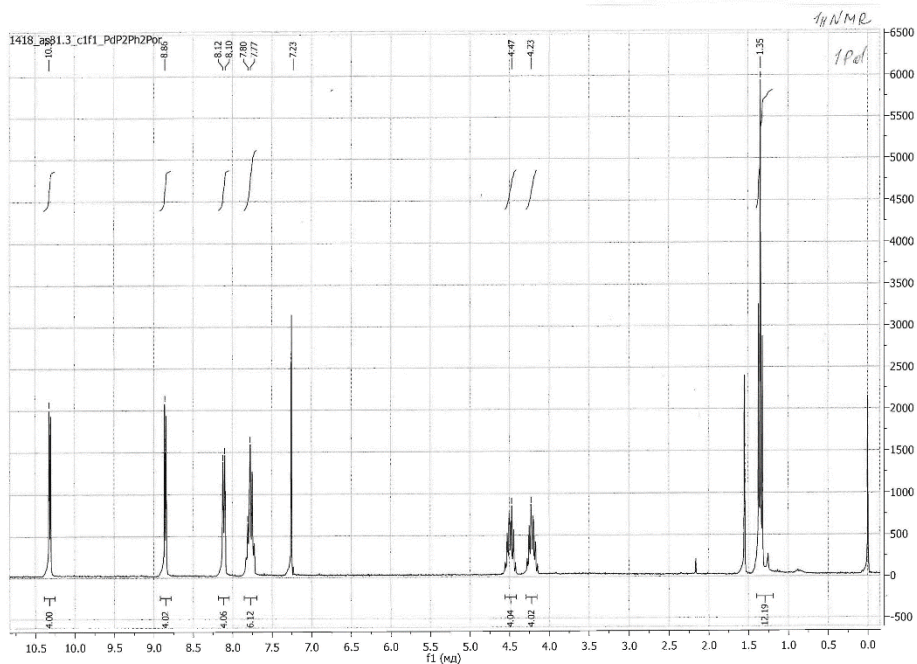


Fig S5 ^1H NMR for **1Pd** (CDCl_3 , 300 MHz, 25 °C)

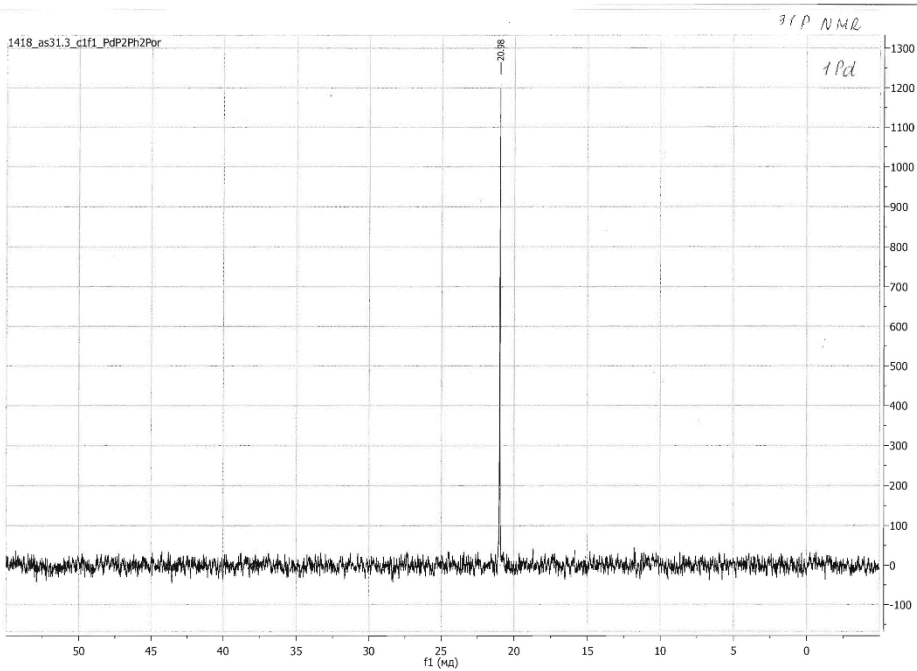


Fig S6 ^{31}P NMR for **1Pd** (CDCl_3 , 121 MHz, 25 °C)

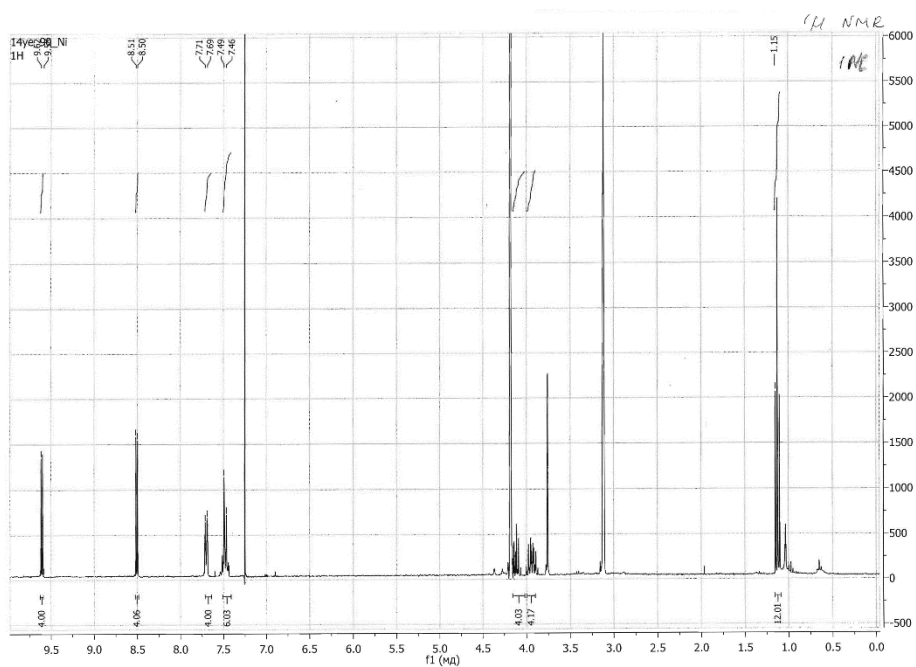


Fig S7 ^1H NMR for **1Ni** ($\text{CDCl}_3/\text{CD}_3\text{OD}$, 2/1 v/v, 300 MHz, 25 °C)

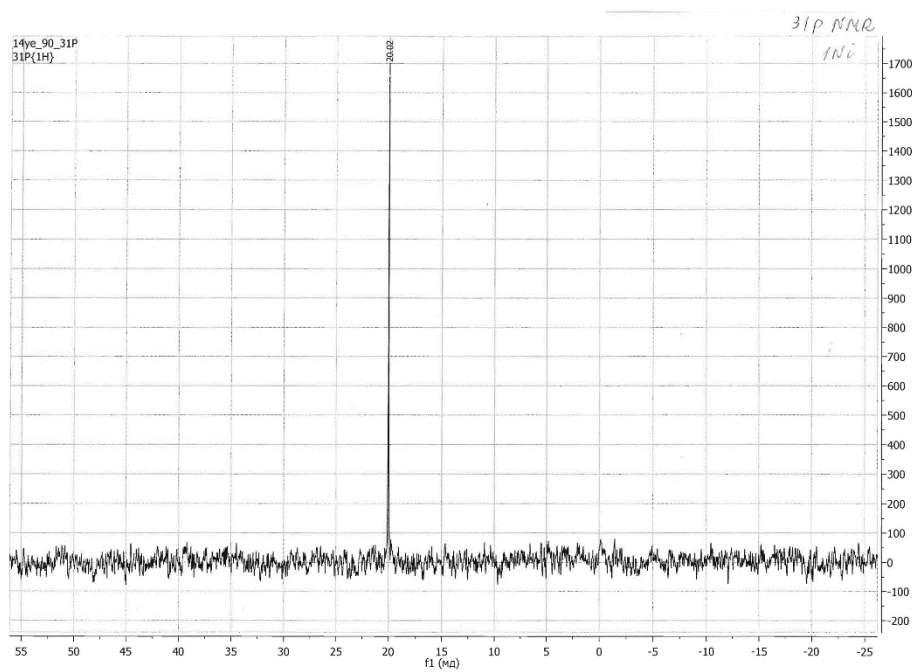


Fig S8 ^{31}P NMR for **1Ni** ($\text{CDCl}_3/\text{CD}_3\text{OD}$, 2/1 v/v, 121 MHz, 25 °C)