Synthesis, crystal packing aspects and pseudosymmetry in coordination compounds with a phosphorylamide ligand

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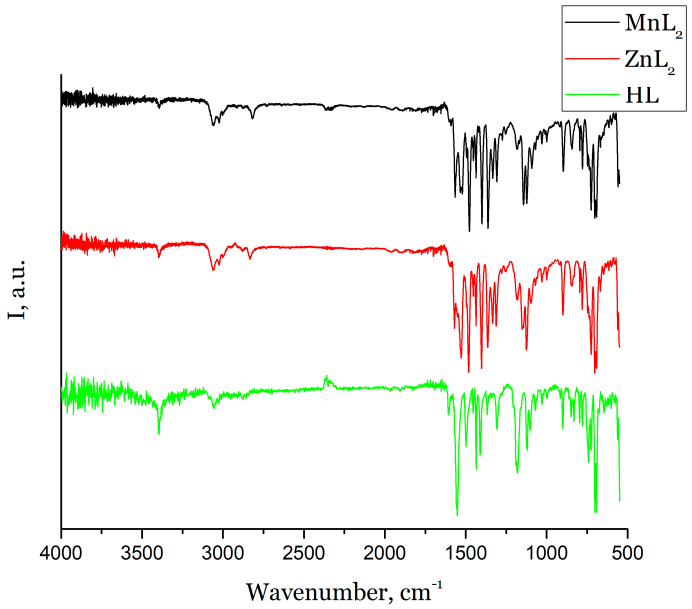


Figure S1. IR spectra of HL (green), **1**·THF (red) and **2**·THF (black)

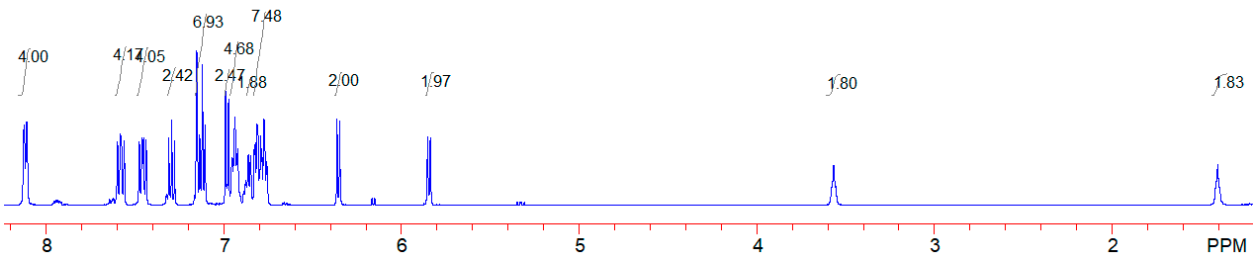


Figure S2. ^{1}H NMR spectrum of **1**·THF in C_6D_6. Minor unlabeled signals are attributed to an impurity of HL.

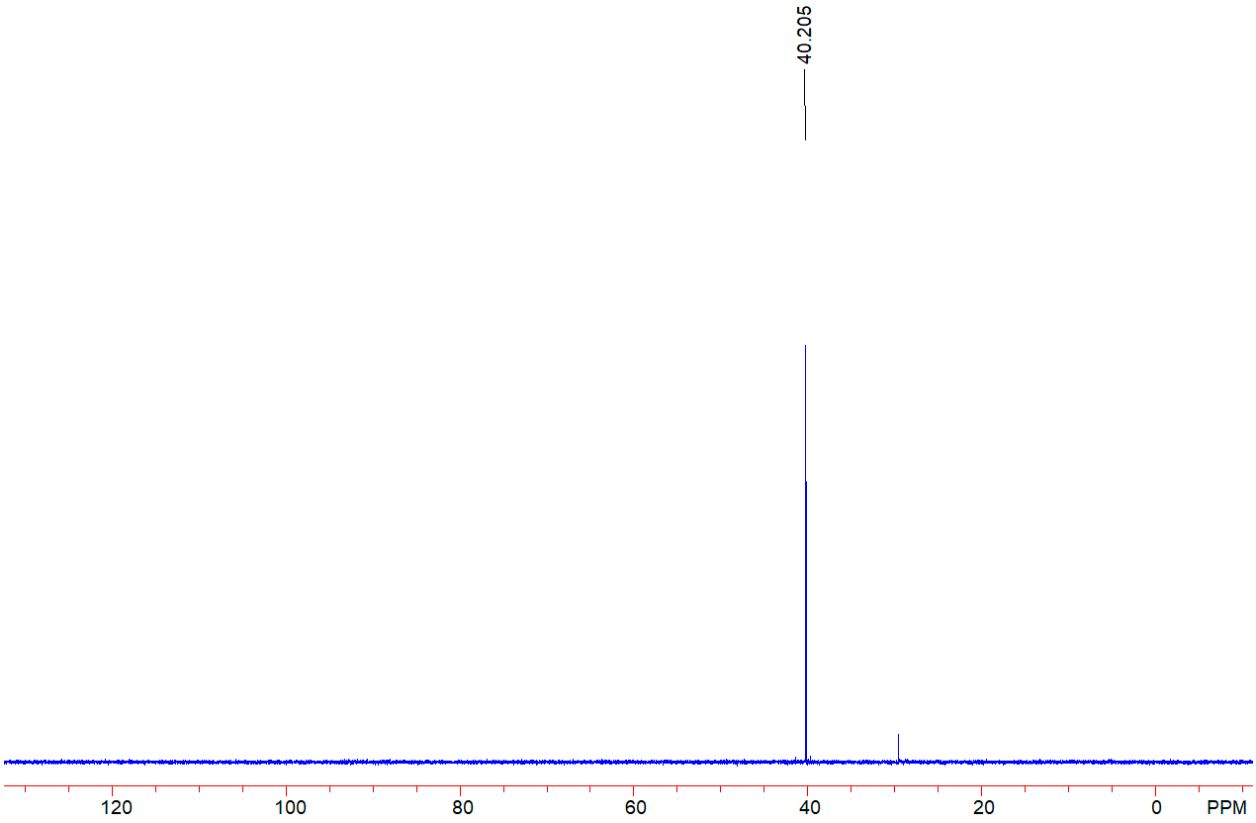


Figure S3. $^{31}P\{H\}$ NMR spectrum of **1**·THF in C_6D_6. Minor unlabelled signal at 29.5 ppm is attributed to an impurity of HL.

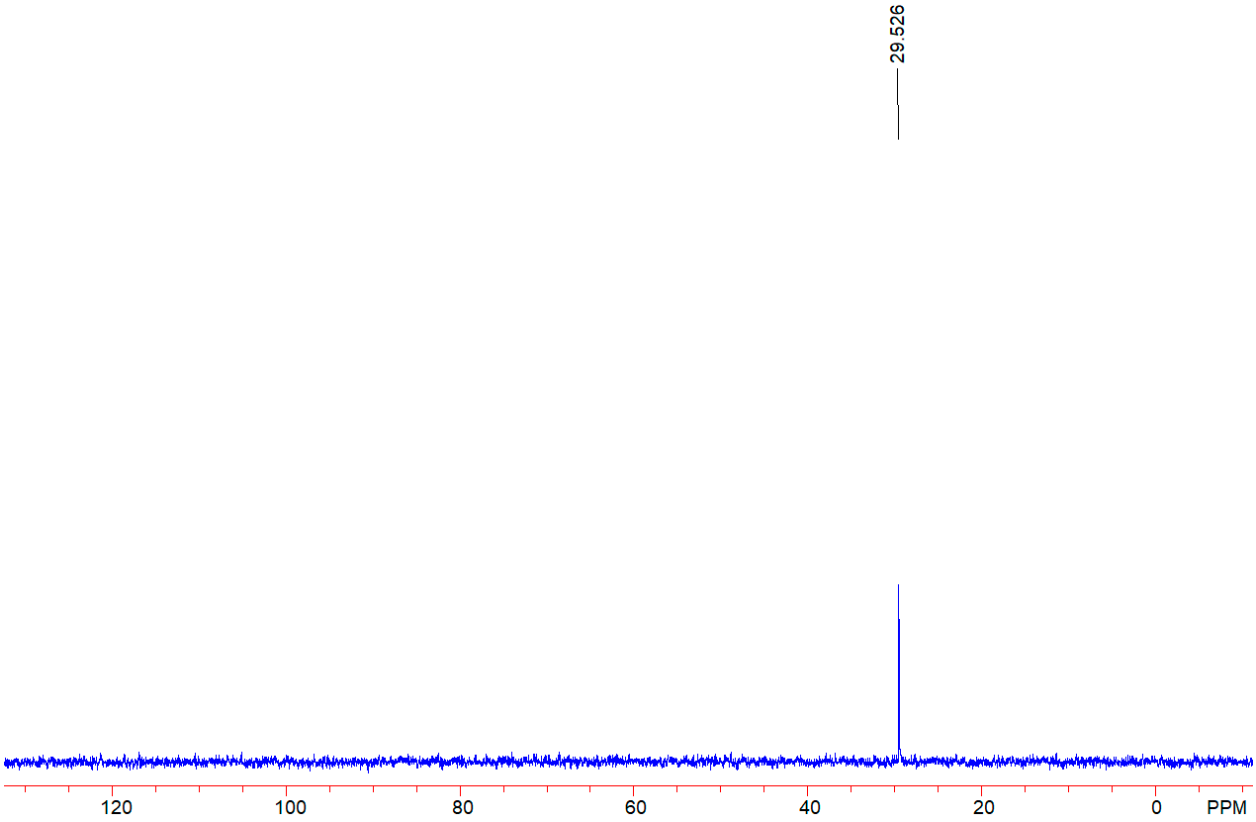
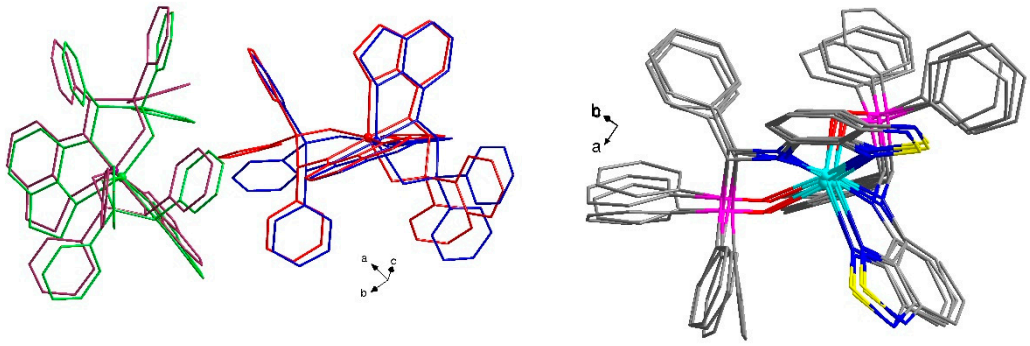


Figure S4. $^{31}P\{H\}$ NMR spectrum of traces of HL obtained at dissolving **2**·THF in C_6D_6.

Table S1. Crystal data and structure refinement for the compounds.

Identification code	**1**·2THF	**2**·THF	**2**·2THF
Empirical formula	$C_{54}H_{46}N_6O_3P_2S_2Zn$	$C_{54}H_{46}MnN_6O_3P_2S_2$	$C_{58}H_{54}MnN_6O_4P_2S_2$
Formula weight	1018.40	1007.97	1080.07
Temperature/K	150(2)	150(2)	150(2)
Space group	$I4_1/a$	$P2_1/c$	$P2_1/c$
a/Å	14.0023(7)	14.1955(7)	16.5442(14)
b/Å	14.0023(7)	48.2164(19)	18.7190(16)
c/Å	48.770(3)	14.1391(5)	17.2449(14)
β/°	90	90.0900(10)	99.847(2)
Volume/Å^3	9562.1(11)	9677.6(7)	5261.9(8)
Z	8	8	4
ρ_{calc} g/cm^3	1.415	1.384	1.363
μ/mm^{-1}	0.720	0.477	0.445
F(000)	4224.0	4184.0	2252.0
Crystal size/mm^3	0.28 × 0.20 × 0.12	0.15 × 0.12 × 0.12	0.16 × 0.16 × 0.05
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.44 to 48.878	3.002 to 48.812	4.332 to 48.812
Index ranges	-16 ≤ h ≤ 13, -10 ≤ k ≤ 14, -40 ≤ l ≤ 56	-16 ≤ h ≤ 12, -56 ≤ k ≤ 55, -16 ≤ l ≤ 16	-19 ≤ h ≤ 19, -21 ≤ k ≤ 21, -20 ≤ l ≤ 20
Reflections collected	15320	48329	77144
Independent reflections	3968 [R_{int} = 0.0578, R_{sigma} = 0.0599]	15896 [R_{int} = 0.0679, R_{sigma} = 0.0803]	8656 [R_{int} = 0.1006, R_{sigma} = 0.0559]
Data/restraints/parameters	3968/6/305	15896/43/1212	8656/33/645
Goodness-of-fit on F^2	1.029	1.015	1.036
Final R indexes [I>=2σ (I)]	R_1 = 0.0453, wR_2 = 0.0969	R_1 = 0.0628, wR_2 = 0.1369	R_1 = 0.0560, wR_2 = 0.1321
Final R indexes [all data]	R_1 = 0.0734, wR_2 = 0.1077	R_1 = 0.1026, wR_2 = 0.1539	R_1 = 0.0887, wR_2 = 0.1509
Largest diff. peak/hole / e Å^{-3}	0.31/-0.33	0.73/-0.63	0.79/-0.63



(a) (b)

Figure S5. Representation of the pseudosymmetry of structure **2**·THF in *I*112/*a* space group (a; adding the two-fold rotational axis) and in $I4_1/a$ space group (b; adding the four-fold rotational axes, as in **1**·2THF).

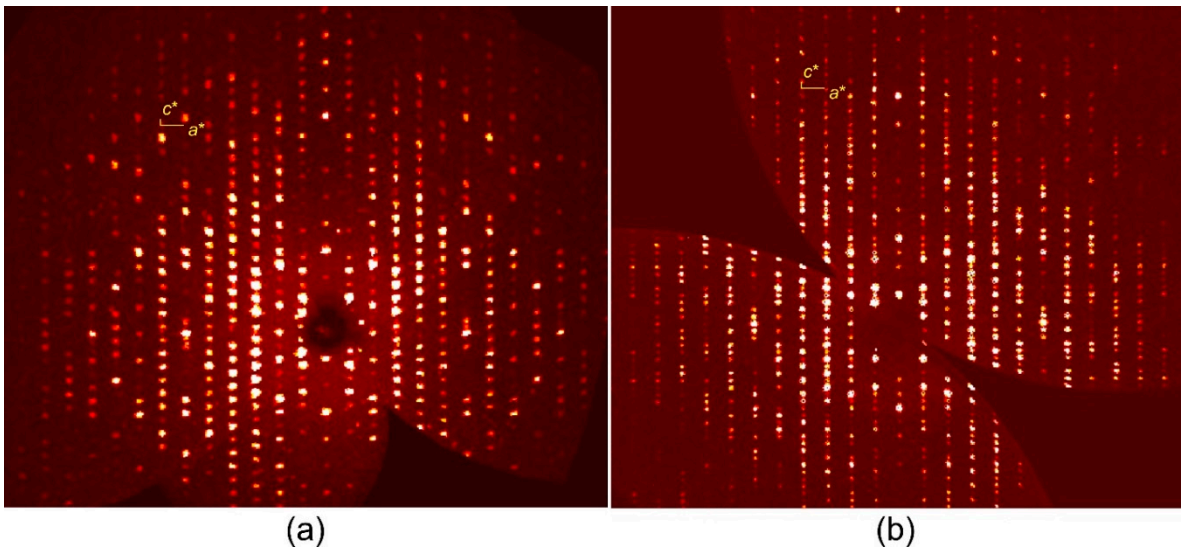


Figure S6. Reciprocal space reconstructions of *h*0*l* layers for **1**·THF (a) and **2**·THF (b; in $P112_1/a$ setting), showing the systematic absences corresponding to the *I* centring ($h+k+l = 2n+1$) and 4_1 screw axis ($h = 0$, $l \neq 4n$) in the former.

Table S2. The Continuous Symmetry Measures (CSM) analysis for the deviation of the coordination polyhedra from the regular octahedron $S(O_h)$ and some geometry parameters of compounds **1**–**2**.

	1·THF	**2**·THF	**2**·2THF	HL (CSD Refcode CEDDOI)
$S(O_h)$	3.78	4.96; 5.01	4.28	–
M–O, Å	2.158(2)	2.191(3); 2.214(3)	2.191(3); 2.208(3)	–
M–N, Å	2.008(3); 2.490(3)	2.155(3); 2.168(3); 2.408(4); 2.437(4)	2.163(3); 2.166(3); 2.354(3); 2.416(3)	–
{N–C–P–O}, deg.	36.8	33.5; 38.8; 39.4; 39.6	37.1; 39.8	61.3

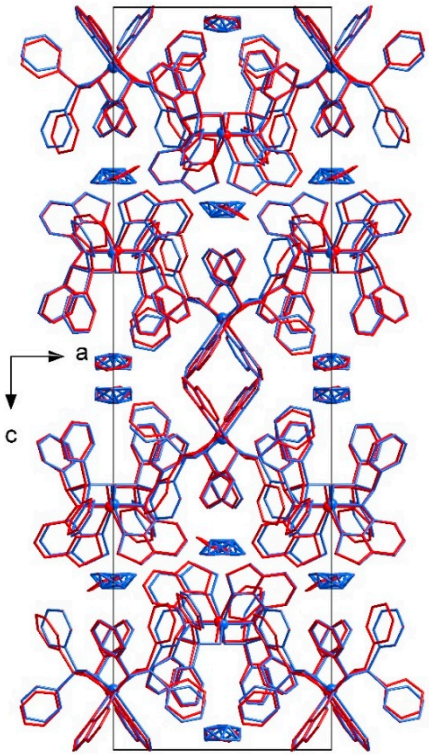


Figure S7. Overlay of crystal packings of **1**·THF (blue) and **2**·THF (red; in $P112_1/a$ setting).

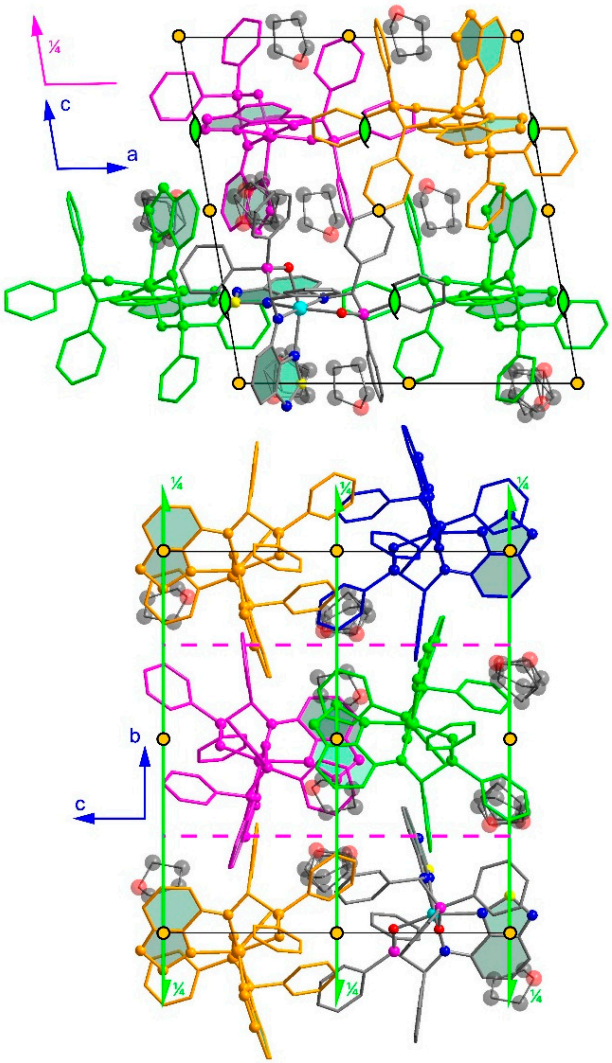


Figure S8. A fragment of crystal packing of compound **2**·2THF showing the symmetry operations. Colour scheme: blue – translation, yellow – inversion, magenta – glide plane, green – 2-fold axis (rotation or screw). Crystallographically independent moiety is shown grey, symmetry-related moieties are coloured with the corresponding symmetry colour scheme. Hydrogen atoms are omitted, solvate THF molecules are shown as transparent spheres (without colours of symmetry relations).

Table S3. Estimated volume of voids in the absence of the THF molecules, intercentroid distance (*C*···*C*) between the neighbouring THF molecules, and the closest intermolecular distance (X···X) between non-hydrogen atoms of the neighbouring THF molecules in the compounds.

	Volume, Å^3	*C*···*C*, Å	X···X, Å
1·THF	159	6.69 7.28 7.87	4.39 5.37 6.44
2·THF (for localized THF1)	316/2 = 158[1]	6.19	4.00
2·THF (for disordered THF2)	334/2 = 167[1]	7.44 7.44 7.66 7.63	5.32 6.05 6.29 5.66
2·2THF (for localized THF1)	127	–[2]	–[2]
2·2THF (for disordered THF2)	153	–[2]	–[2]

[1] – the void is coupled

[2] – no close contacts

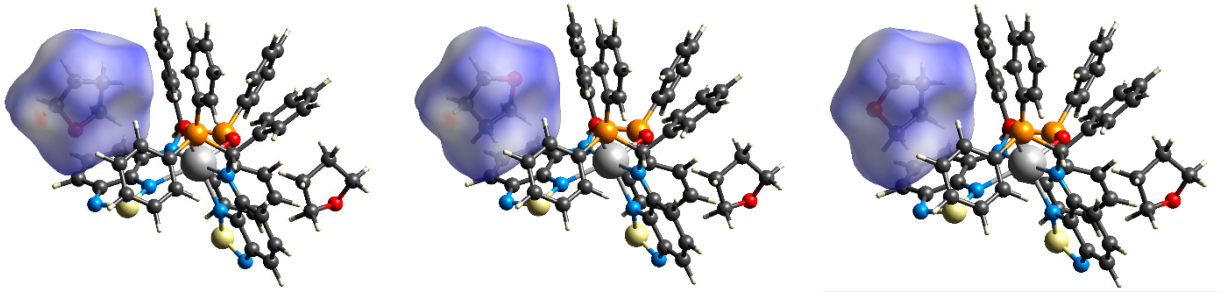


Figure S9. Hirshfeld surfaces of different variants of arrangement of the THF molecule in **2**·2THF. Colour mapping scheme on the surfaces: regions with the distances between atoms less than the sum of their van der Waals radii are shown red; regions with the distances equal to the sum of van der Waals radii are white, regions with the distances larger than the sum of van der Waals radii are blue. The surface mapping range: –0.2/1.5 a.u.