Electronic Supplementary Information

Metal ion-assisted transformations of 2-pyridinealdoxime and hexafluorophosphate†

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Compounds' Syntheses

[Zn(NO$_3$)(paoH)(picH)](NO$_3$) (1). A solution of $Zn(NO_3)_2\cdot4H_2O$ (261 mg, 1.00 mmol) in MeOH (7 mL) was added to a stirred solution of paoH (244 mg, 2.00 mmol) in the same solvent (5 mL). The resulting pale yellow solution was refluxed for 3 h and stored in a closed vial. After 4 d, colourless crystals of the product formed in 55% yield. The crystals were collected by filtration, washed with cold MeOH (1 mL) and Et_2O (2x5 mL), and dried in air. Elemental analyses: Calcd for $C_{12}H_{11}N_5O_9Zn$ (found): C, 33.16 (32.99); H, 2.56 (2.49); N, 16.12 (16.20) %. IR bands (KBr): 3349m, 3160mb, 3081w, 1680s, 1589m, 1572s, 1493sh, 1452sh, 1433s, 1310s, 1276m, 1184w, 1168w, 1130m, 1102w, 1054sh, 1044m, 1027s, 907w, 818m, 786m, 755s, 707w, 667m, 651s, 604mb, 511w cm^{-1}.

[ZnL$_2$(H$_2$O)$_2$](NO$_3$)$_2$ (2; L=picolinamide). Solid paoH (391 mg, 3.20 mmol) was slowly added to a solution of $Zn(ClO_4)_2\cdot6H_2O$ (296 mg, 0.79 mmol) and $Tb(NO_3)_3\cdot6H_2O$ (362 mg, 0.80 mmol) in MeCN (25 mL). The resulting pale yellow solution was stirred for 2 h at room temperature and stored in a closed vial. After 5 d, X-ray quality colourless crystals of the product were precipitated. The crystals were collected by filtration, washed with MeCN (2x1 ml) and Et_2O (2 x 5 mL), and dried in air. The yield was ~50% (based on the Zn^{II} available). Elemental analyses: Calcd for $C_{12}H_{16}N_6O_{10}Zn$ (found): C, 30.68(30.80); H, 3.44(3.37); N, 17.90(17.52)%. IR bands (KBr): 3299mb, 3140mb, 3030sh, 2945w, 1660s, 1582s, 1566vs, 1473s, 1434s, 1385m, 1354w, 1312sh, 1297m, 1262sh, 1170w, 1160w, 1121m, 1095w, 1052w, 1033m, 1011m, 959w, 818m, 788m, 749m, 680s, 659sh, 650s, 633m, 621w, 610w, 520m cm^{-1}.

[Zn$_2$(PO$_3$F)$_2$(paoH)$_4$] (3). An aqueous solution (15 mL) of $ZnCl_2$ (136 mg, 1.00 mmol) was slowly added to an aqueous solution (30 mL) of paoH (244 mg, 2.00 mmol) and $NaPF_6$ (335 mg, 1.99 mmol). The resulting colourless solution was stirred for 10 min, filtered and stored in a closed vial. After one month, colourless crystals of the product formed. The crystals were collected by filtration, washed with H_2O (2x1 mL), EtOH (2x1 mL) and Et_2O (2x3 mL), and dried in air. The yield was 40% (based on the available Zn^{II}). Calcd for $C_{24}H_{24}N_8O_{10}P_2F_2Zn$ (found): C, 35.36(35.53); H, 2.97(3.09); N, 13.75(13.70) %. IR bands (KBr): 3448mb, 3178w, 3084w, 2889w, 1602s, 1508s, 1500sh, 1495m, 1458w, 1437w, 1331m, 1306m, 1260w, 1221sh, 1191m, 1153sh, 1112m, 1042s, 1017s, 948w, 891m, 846s. 777m, 746w, 677w, 641w, 558s, 515m, 491w cm^{-1}. NMR data in DMSO-d$_6$: ^{19}F: δ_F = -75.3 ppm, d, J_{P-F} = 922 Hz; ^{31}P NMR: δ_P = -8.3 ppm, d, J_{P-F} = 922 Hz). It should be noted that the molar conductivity value of a 10^{-3} M solution of **3** in DMSO at 25 ^{o}C is 72 S cm^2 mol^{-1}, probably indicating decomposition of the complex in solution and liberation of PO_3F^{2-} in solution. In agreement with this view, the ^{19}F and ^{31}P NMR spectra in DMSO-d$_6$ are very close to those reported for salts containing the PO_3F^{2-} ion [see ref. 24b of the Communication and also: R. Fernández-Galán, B. R. Manzano, A. Otero, M. Lanfranchi and M. A. Pellinghelli, *Inorg. Chem.*, 1994, **33**, 2309].

X-Ray Crystallography - Experimental

Data for a selected small (0.08x0.05x0.03 mm) colourless plate of complex **1** were collected at Station 11.3.1 of the Advanced Light Source at Lawrence Berkeley National Laboratory (USA), using a Bruker APEX II CCD diffractometer [synchrotron radiation at 0.7749 Å from a silicon (111) monochromator]. The data were corrected for absorption with SADABS[1], and the structure was solved with SIR97[2] and refined against F^2 with SHELXL97.[1] All non-H atoms were refined anisotropically and all H atoms, including those on O1 and O3 (see Fig. 1) were found in difference Fourier maps. These were nevertheless placed geometrically and refined with a riding model.

Data for a selected, colourless block (0.35x0.28x0.24 mm) of complex **2** were collected on a Stoe IPDS II area detector diffractometer using graphite-monochromated Mo-K*a* radiation in the Institute of Nanotechnology, Karlsruhe Institute of Technology (Germany). The structure was solved by direct methods using the *SHELXS-97*[3] program with the *WinGX*[4] graphical user interface, followed by a full-matrix least squares refinement against F^2 using SHELXTL.[5] A semi-empirical correction (*SADABS*[6]) was applied. Anisotropic refinement was used for all ordered non-H atoms. Organic H atoms were placed at calculated positions, while the H_2O and -NH_2 H atoms were located in difference Fourier maps and then constrained to ride on their parent atom with $U_{iso} = 1.2\ U_{eq}$(parent atom).

Data for complex **3** were collected (ω scans) on an Oxford Diffraction Xcalibur-3 diffractometer under a flow of nitrogen gas using graphite-monochromated Mo-Kα radiation in the Chemistry Department of the University of Cyprus at Nicosia. A suitable single crystal (0.32x0.24x0.14 mm) was covered with Paraton-N oil and attached on the tip of a glass capillary. Data collection and reduction was performed with CrysAlis CCD and RED software,[7] respectively. The reflection intensities were corrected for absorption by the multi-scan method. The structure was solved by direct methods with SIR92 [8] and refined by full-matrix least-squares on F^2 with SHELXL-97[9]. All non-H atoms were refined anisotropically. Organic H atoms were introduced at calculated positions applying the riding model [$C(sp^2)$–H = 0.93 Å; $U_{iso}(H) = 1.2U_{eq}(C)$ of their carrier C atom]. The oxime H atoms [HO1 and HO2] were found in a difference Fourier map and refined isotropically [$U_{iso}(H) = 1.5U_{eq}(O)$] applying a soft distance restraint for HO2 atom. Geometric calculations were carried out using WINGX[10] and PLATON[11] packages; molecular graphics were prepared with DIAMOND[12].

1 G. M. Sheldrick, SHELXTL, Bruker AXS Inc., Madison, WI, 2004.

2 A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori and R. Spagna, *J. Appl. Crystallogr.*, 1999, **32**, 115.

3 G. M. Sheldrick, *SHELXL-97*: *Program for Solution of Crystal Structures*, University of Göttingen, Germany, 1997.

4 L. J. Farrugia, *J. Appl. Crystallogr.*, 1997, **30**, 565.

5 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 2008, **64**, 112.

6 R. H. Blessing, *Acta Crystallogr., Sect. A*, 1995, **51**, 33.

7 *CrysAlis CCD and CrysAlis RED*, Oxford Diffraction Ltd, Abingdon, Oxford, UK, 2009.

8 A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori and M. Camalli, *J. Appl. Crystallogr.*, 1994, **27**, 435.

9 G. M. Sheldrick, *SHELXL-97*: *Program for the Refinement of Crystal Structures from Diffraction Data*, University of Göttingen, Germany, 1997.

10 L. J. Farrugia, *J. Appl. Crystallogr.*, 1999, **32**, 837.

11 A. L. Spek, *PLATON*, *A Multipurpose Crystallographic Tool*, Utrecht University, The Netherlands, 2008.

12 K. Brandenburg, *DIAMOND, Program for Crystal and Molecular Structure Visualization*, Crystal Impact GbR, Bonn, Germany, 2011.

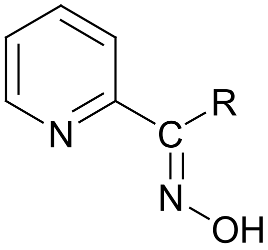

Fig. S1 General structural formula of simple 2-pyridyl oximes (R=H, Me, Ph, 2-pyridyl, NH_2, CN,...). The ligand discussed in the present Communication is 2-pyridinealdoxime (R=H; paoH).

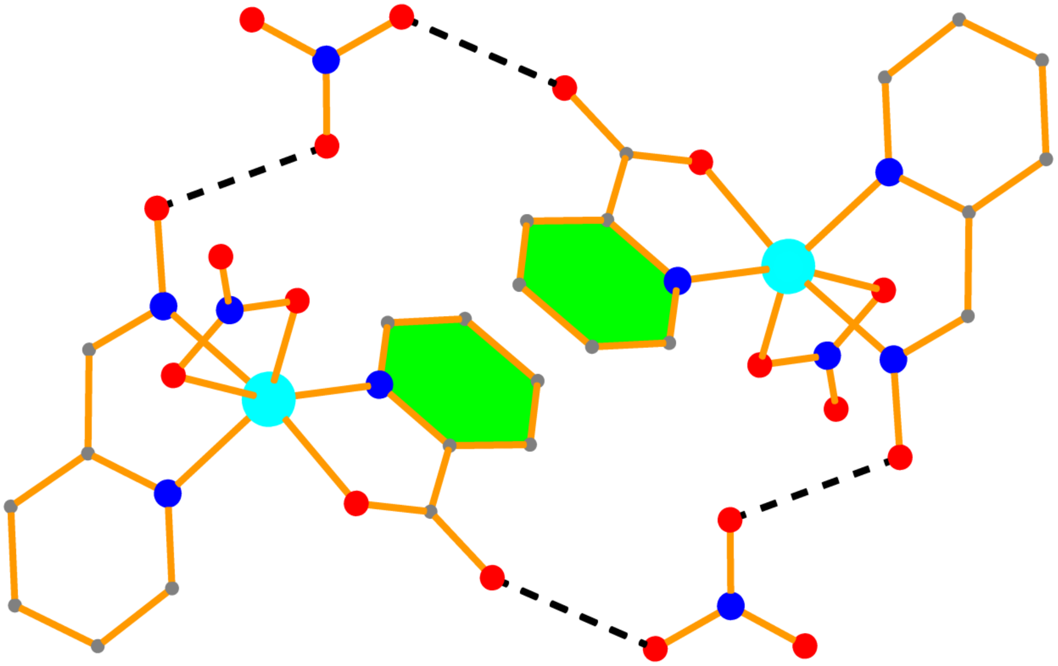

Fig. S2 The “tetramer” $\{[Zn(NO_3)(paoH)(picH)]_2(NO_3)_2\}$ created by hydrogen bonds (dashed lines) and π-π stacking interactions (between the highlighted picolinate aromatic rings) in the crystal structure of **1**.

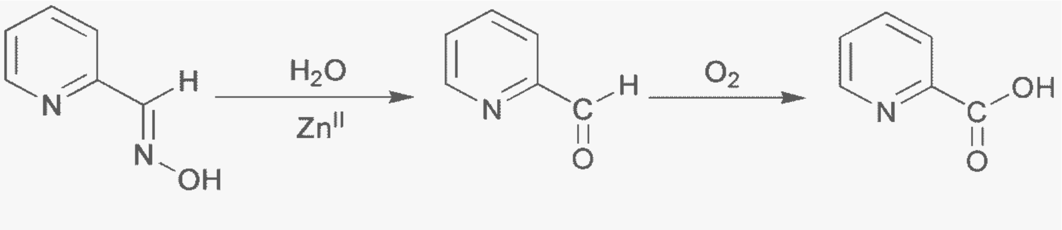

Fig. S3 A simplified view for the transformation of 2-pyridinealdoxime (paoH) to picolinic acid (picH) during the preparation of complex **1**. The hydrolysis involves[15] the reaction of the electrophilically activated, coordinated oxime group with H_2O. Aldehydes can be oxidised to carboxylic acids by atmospheric oxygen, but the actual direct oxidation product may be the picolinic peroxy acid [(py)CO_3H], which comproportionates with another molecule of paoH to give two molecules of picH [M. B. Smith and J. March, *Advanced Organic Chemistry*, 5th ed., Wiley, New York, 2001].

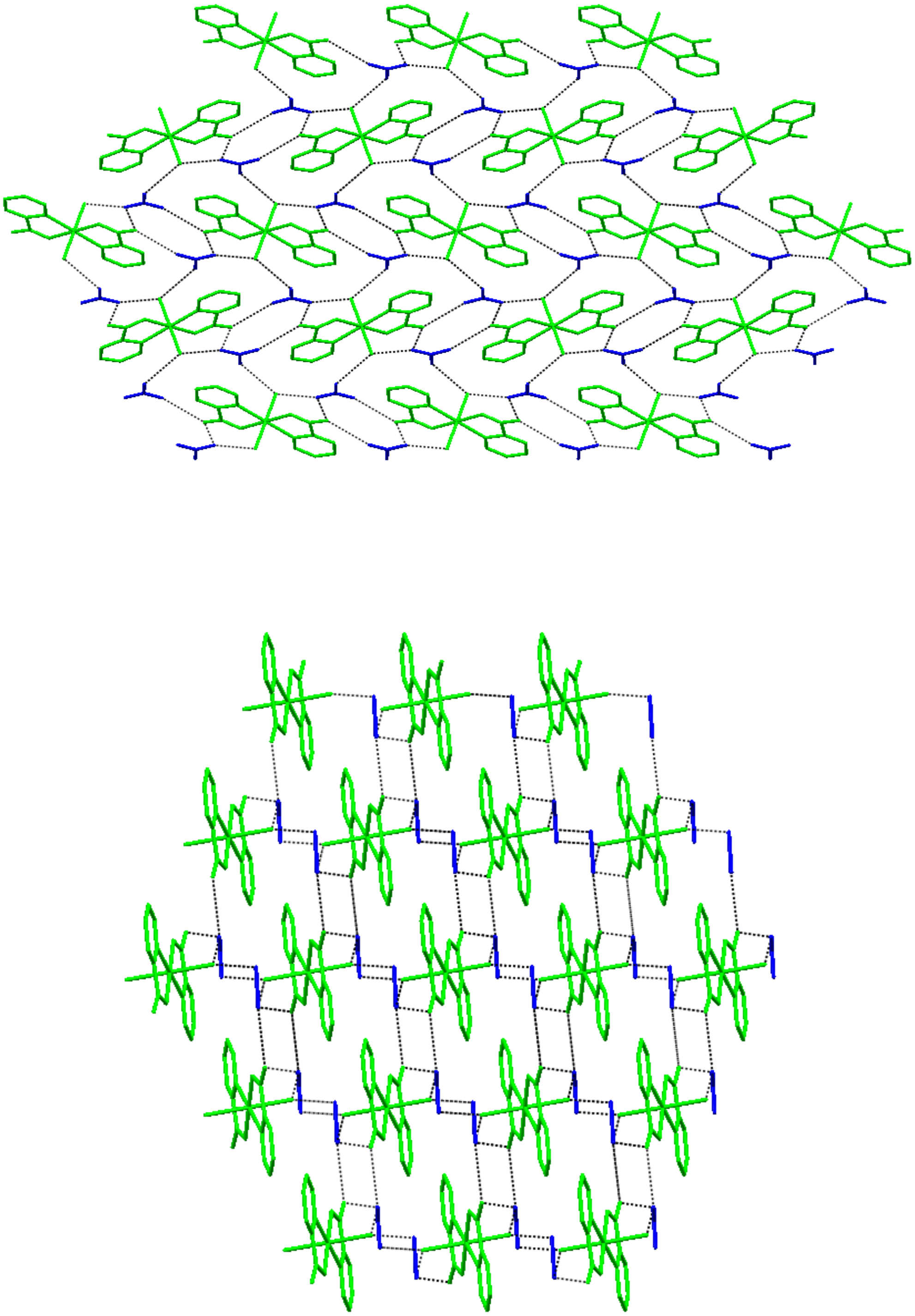

Fig. S4 The H-bonded 2D network in the crystal structure of **2** viewed along the *a* (top) and *b* (down) axes.

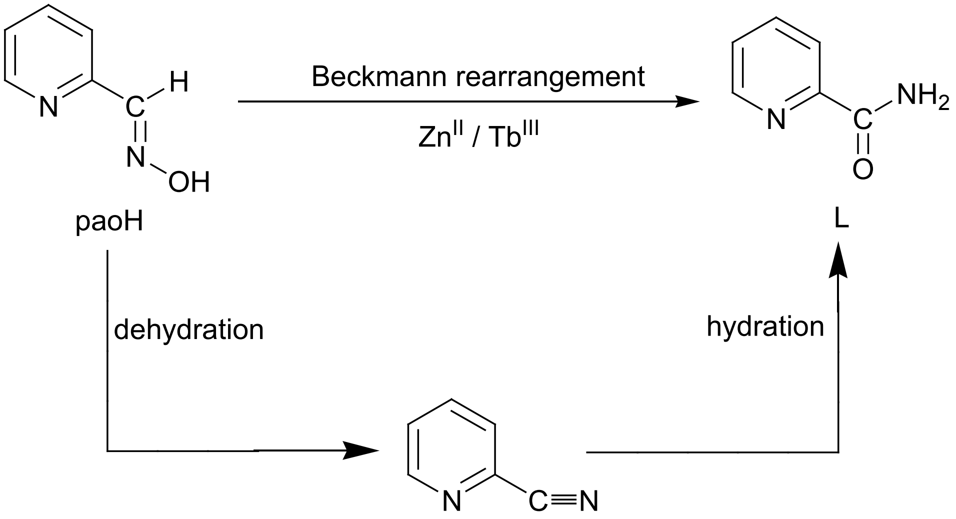

Fig. S5 A simplified view for the transformation of 2-pyridinealdoxime (paoH) to picolinamide (L) during the preparation of **2**. This view is based on the currently available information[7,19] for the metal-ion-catalysed rearrangement of aldoximes to primary amides.

Table S1 Crystallographic data for complexes **1, 2** and **3**

	1	**2**	**3**
Formula	$C_{12}H_{11}N_5O_9Zn$	$C_{12}H_{16}N_6O_{10}Zn$	$C_{24}H_{24}N_8O_{10}P_2F_2Zn_2$
M_w/g mol^{-1}	434.63	469.68	815.23
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/n$
a/Å	7.6874(12)	6.8777(6)	9.1885(3)
b/Å	9.9484(16)	11.2057(11)	12.1035(5)
c/Å	11.4223(17)	12.8526(12)	13.9159(5)
α/°	96.449(3)	90	90
β/°	96.478(4)	113.523(7)	90.663(3)
γ/°	11.272(4)	90	90
V/Å^3	797.6(2)	908.23(15)	1547.53(10)
Z	2	2	2
T/ K	150(2)	180(2)	100(2)
λ/Å	0.77490 [a]	0.71073 [b]	0.71073 [b]
D_c/g cm^{-3}	1.810	1.717	1.749
μ/mm^{-1}	2.022	1.420	1.734
$F(000)$	440	480	824
θ *range*/°	1.98-28.99	2.51-26.75	3.13-28.00
Measd reflns	5343	5330	12593
Unique reflns (R_{int})	3182 (0.0304)	1900 (0.0210)	3695 (0.0180)
Observed reflns [$I>2\sigma(I)$]	2768	1706	3031
$R1$[c]	0.0409	0.0241	0.0218
wR2[d,e]	0.1096	0.685	0.0582
GOF on F^2	1.056	1.054	1.024
$(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$/e Å^{-3}	0.771, -0.500	0.232, -0.213	0.310, -0.394

[a] Synchrotron radiation. [b] Mo Ka radiation. [c] $R1 = \Sigma(|F_o|-|F_c|)/\ \Sigma(|F_o|)$ for observed reflections. [d] $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = [\max(F_o^2, 0) + 2F_c^2]/3$. [e] $wR2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\ \Sigma[w(F_o^2)^2]\}^{1/2}$ for all data.

Table S2 Selected bond lengths (Å) and angles (°) for complex **1**

Zn1-O2	2.065(2)	O2-Zn1···O4	98.2(1)
Zn1···O4	2.473(3)	O2-Zn1-N1	171.6(1)
Zn1-O5	2.071(3)	O2-Zn1-N3	79.6(1)
Zn1-N1	2.187(2)	O4···Zn1-O5	55.3(1)
Zn1-N2	2.054(3)	O4-Zn1-N3	158.3(1)
Zn1-N3	2.055(2)	O5-Zn1-N2	141.0(1)
C7[a]-O2	1.246(4)	N1-Zn1-N2	77.0(1)
C7[a]-O3	1.320(4)	O2- C7[a]-O3	121.7(3)
N4-O4	1.250(4)	O4-N4-O5	116.8(3)
N4-O5	1.261(4)	O5-N4-O6	122.6(3)
N4-O6	1.216(4)	O5-N4-O6	120.6(3)

[a] Atom C7 belongs to the carboxylic group of picolinic acid (picH); this atom is not labelled in Fig. 1.

Table S3 Selected bond lengths (Å) and angles (°) for complex **2**[a]

Zn1-O1	2.073(1)	O1-Zn1-O2	89.6(1)
Zn1-O2	2.123(2)	O1-Zn1-N2	78.6(1)
Zn2-N2	2.098(1)	O1-Zn1-N2'	101.4(1)
C1[b]-O1	1.243(2)	O1-C1[b]-N1	122.3(2)
C1[b]-N1	1.308(2)		

[a] Symmetry code: (‘) = 1 - *x*, - *y*, - *z*. [b] Atom C1 belongs to the primary amide group; this atom is not labelled in Fig. 2.

Table S4 Selected interatomic distances (Å) and angles (°) for complex **3**[a]

Zn-O3	1.998(1)	O3-Zn-O4	98.0(1)
Zn-O4	2.015(1)	O3-Zn-N3	170.2(1)
Zn-N1	2.175(1)	O4-Zn-N1	167.8(1)
Zn-N2	2.220(1)	O4-Zn-N3	88.9(1)
Zn-N3	2.231(1)	N1-Zn-N2	74.3(1)
Zn-N4	2.203(1)	N1-Zn-N4	90.6(1)
P-O3	1.495(1)	N2-Zn-N4	162.4(1)
P-O4’	1.510(1)	N3-Zn-N4	74.6(1)
P-O5	1.517(1)	O3-P-O5	114.7(1)
P-F	1.585(1)	O4-P’-F’	103.4(1)
Zn···Zn’	5.080(3)	O5-P-F	105.0(1)

[a] Symmetry code: (‘) = - *x*, - *y*, - *z*.