Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Complex formation of copper(II), nickel(II) and zinc(II) with ethylphosphonoacetohydroxamic acid: solution speciation, synthesis and structural characterization

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Supplementary Information

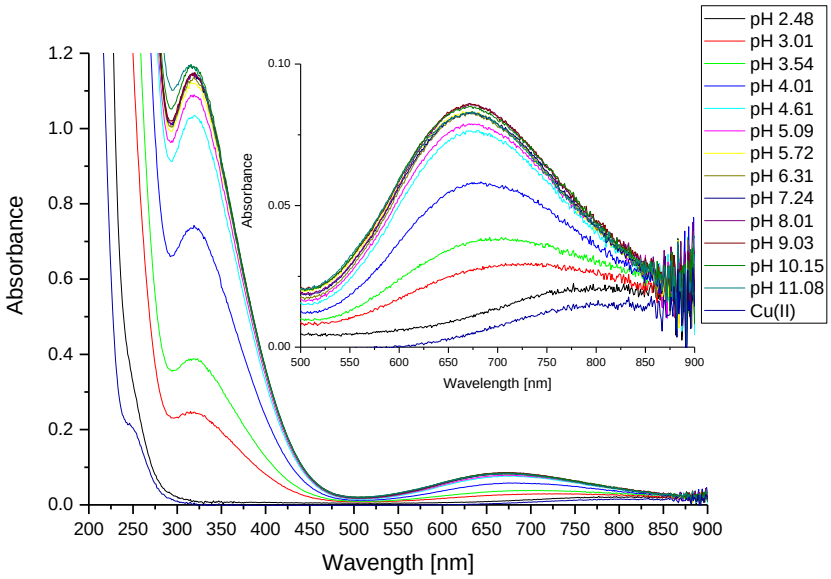

Figure S1. pH-dependent changes of UV-Vis spectra of Cu(II)/**PAHEt** system, [L] = $3.33 \cdot 10^{-3}$ M, metal-to-ligand ratio of 1:3, l = 1cm.

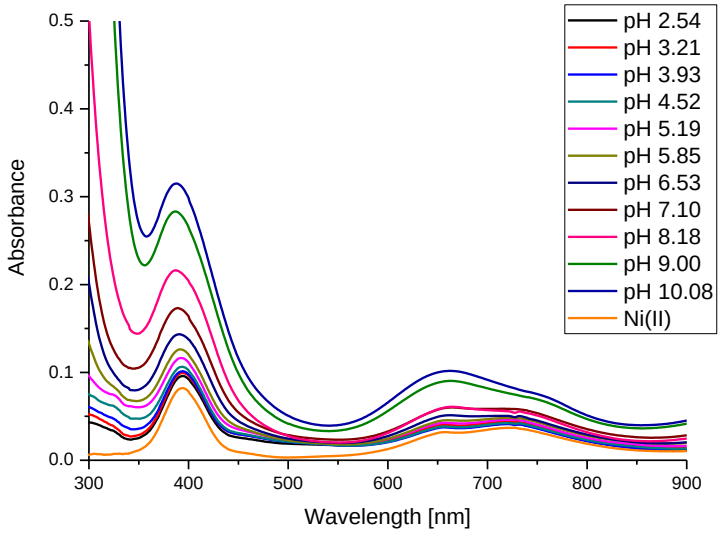

Figure S2. pH-dependent changes of UV-Vis spectra of Ni(II)/**PAHEt** system, [L] = $5.68 \cdot 10^{-3}$ M, metal-to-ligand ratio of 1:3, l = 5cm.

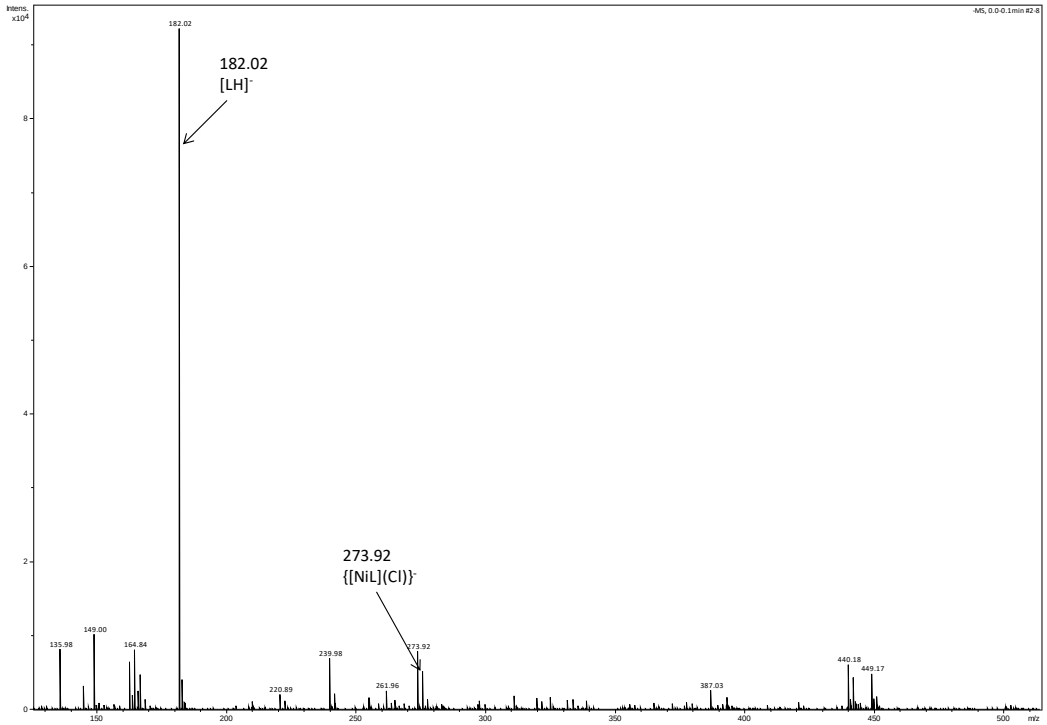

Figure S3. ESI-MS spectra of Ni(II)/**PAHEt** system, metal-to-ligand ratio of 1:1 at pH 8.

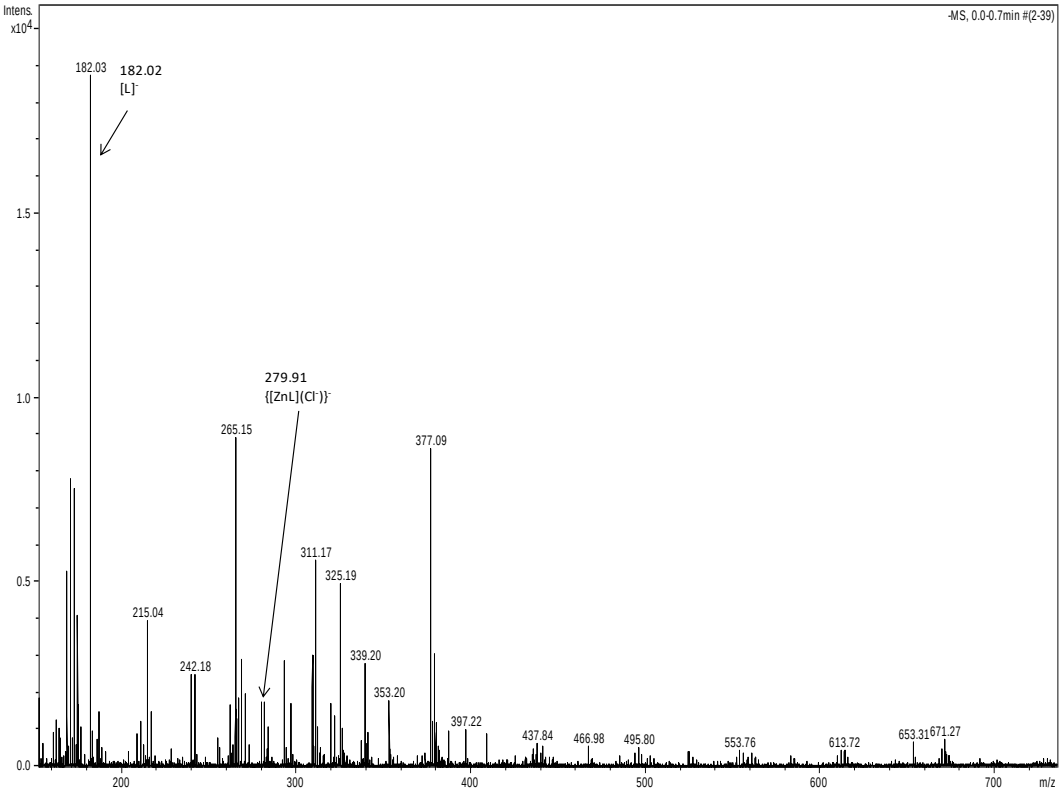

Figure S4. ESI-MS spectra of Zn(II)/**PAHEt** system, metal-to-ligand ratio of 1:1 at pH 8.

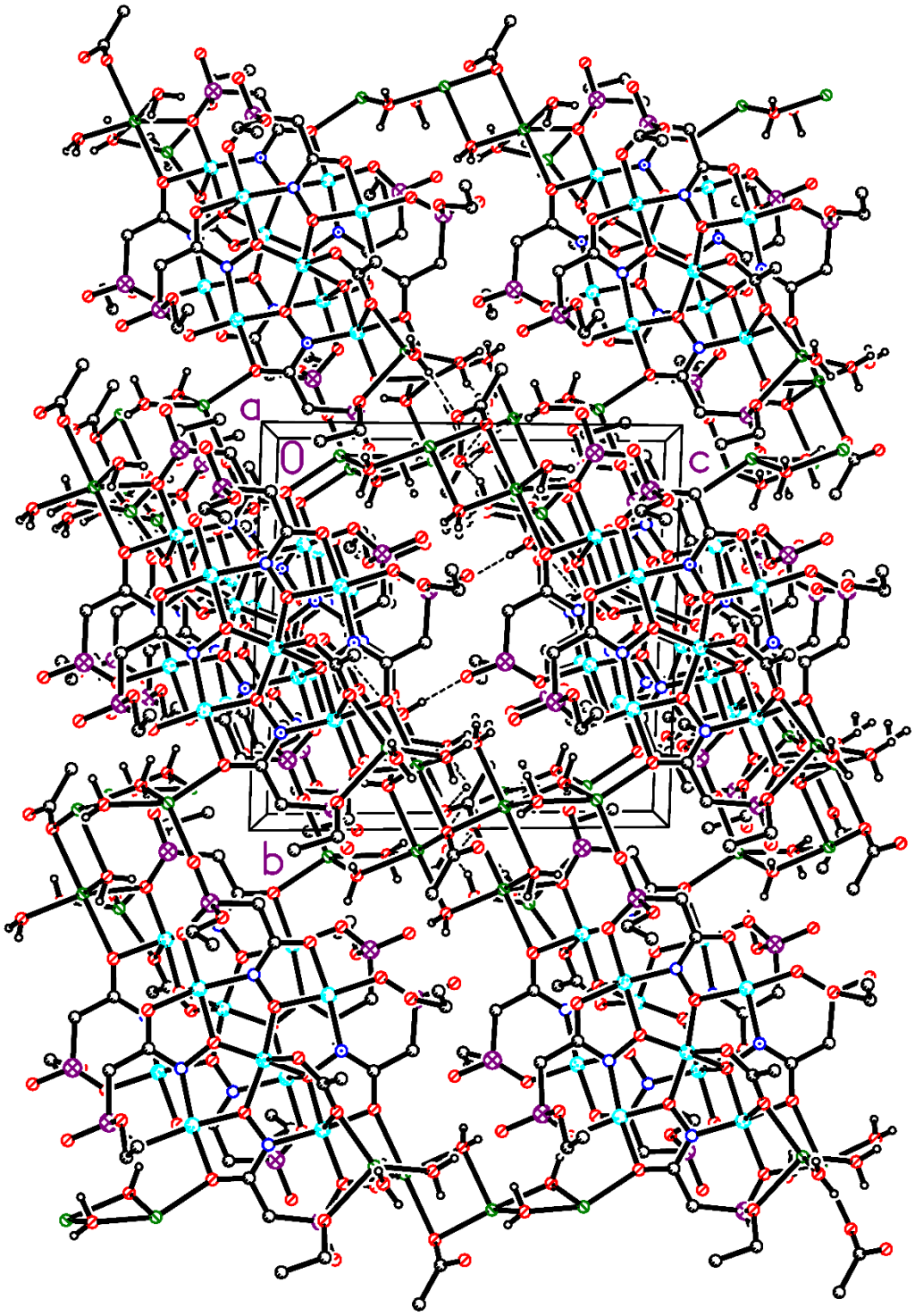

Figure S5. Packing diagram for **1** (a view along *a* direction of the crystal). Hydrogen atoms not involved into H-bonds and minor fractions of the disordered atoms are omitted for clarity. Colour scheme: turquoise = Cu, red = O, blue = N, black = C and H, purple = P, green = Na. H-bonds are represented by dashed lines.

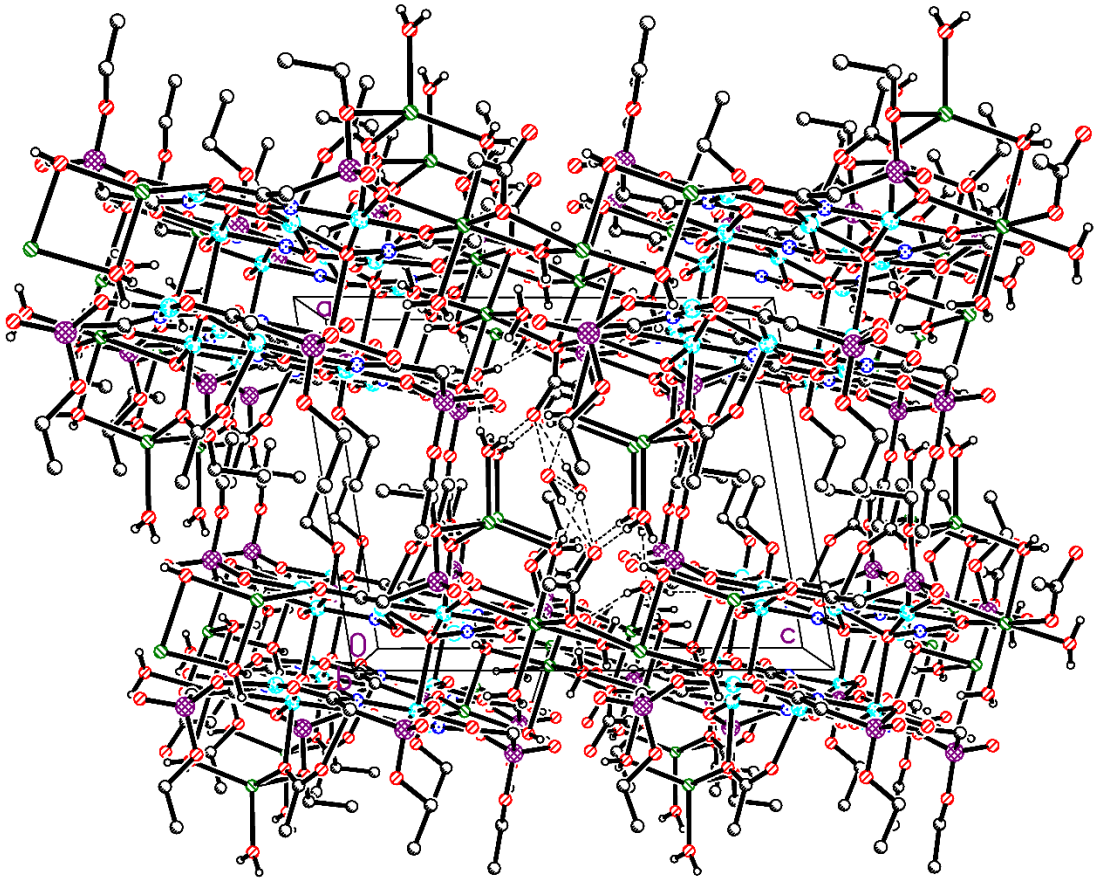

Figure S6. Packing diagram for **1** (a view along *b* direction of the crystal). Hydrogen atoms not involved into H-bonds and minor fractions of the disordered atoms are omitted for clarity. Colour scheme: turquoise = Cu, red = O, blue = N, black = C and H, purple = P, green = Na. H-bonds are represented by dashed lines.

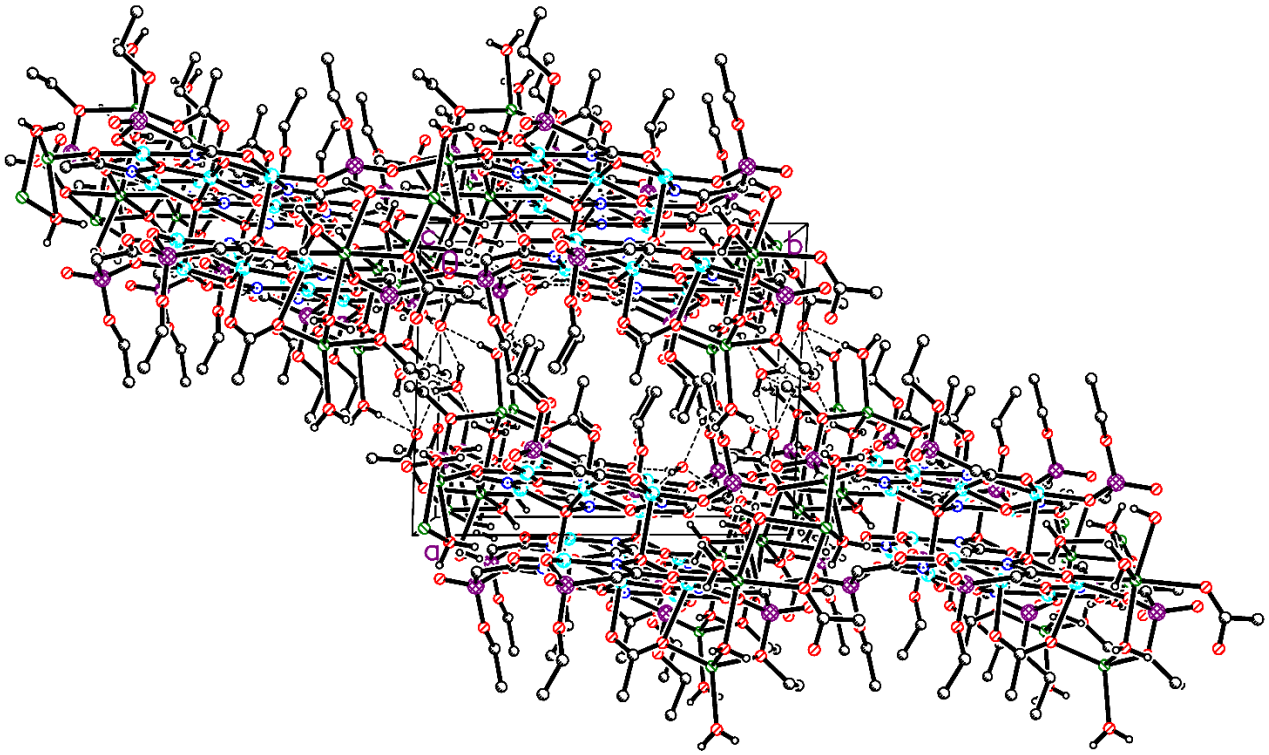

Figure S7. Packing diagram for **1** (a view along *c* direction of the crystal). Hydrogen atoms not involved into H-bonds and minor fractions of the disordered atoms are omitted for clarity. Colour scheme: turquoise = Cu, red = O, blue = N, black = C and H, purple = P, green = Na. H-bonds are represented by dashed lines.

Table S1. Crystal data and structure refinement parameters for the X-ray structure of **1**.

Crystal data

$2(C_{20}H_{46}Cu_5N_4Na_4O_{30}P_4)\cdot 3(H_2O)$	$F(000)$ = 1396
M_r = 2766.34	
Triclinic, *P-1*	D_x = 1.970 Mg m^{-3}
Hallsymbol: ?	
a = 11.5160 (3) Å	Mo$K\alpha$ radiation, λ = 0.71073 Å
b = 13.9940 (3) Å	
c = 14.6740 (2) Å	θ = 1.0–27.5°
α = 91.470 (1)°	μ = 2.52 mm^{-1}
β = 99.155 (1)°	T = 100 K
γ = 91.943 (1)°	Needle, green
V = 2332.17 (9) Å^3	0.22 × 0.10 × 0.09 mm
Z = 1	

Data collection

NoniusKappaCCD diffractometer	10669 independent reflections
Radiation source: fine-focus sealed tube	8022 reflections with $I > 2\sigma(I)$
Horizontally mounted graphite crystal monochromator	R_{int} = 0.051
Detector resolution: 9 pixels mm^{-1}	θ_{max} = 27.5°, θ_{min} = 2.6°
φ scans and ω scans with κ offset	h = −14 14
Absorption correction: multi-scan *SORTAV* (Blessing, 1995)	k = −18 18
T_{min} = 0.596, T_{max} = 0.795	l = −17 19
45451 measured reflections	

Refinement

Refinement on F^2	
Least-squares matrix: full	Hydrogen site location: mixed
$R[F^2 > 2\sigma(F^2)]$ = 0.041	H-atom parameters constrained
$wR(F^2)$ = 0.109	$w = 1/[\sigma^2(F_o^2) + (0.0475P)^2 + 5.3531P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.02	$(\Delta/\sigma)_{max}$ = 0.001
10669 reflections	$\Delta\rho_{max}$ = 1.96 e Å^{-3}
648 parameters	$\Delta\rho_{min}$ = −0.65 e Å^{-3}
6 restraints	

Table S4. Bond lengths (Å) and angles (°) for **1**.

Cu1—O2	1.901 (3)	O9—C12	1.302 (4)
Cu1—O21^{i}	1.926 (3)	O11—C8	1.296 (4)
Cu1—O1	1.955 (3)	O13—C3B	1.308 (18)
Cu1—N1	1.971 (3)	O13—C3A	1.429 (7)
Cu1—O6^{ii}	2.439 (3)	O16—C6	1.457 (6)
Cu2—O3	1.864 (2)	O18—H18O	0.9498
Cu2—O12	1.900 (3)	O18—H18P	0.9430
Cu2—O11	1.947 (2)	O19—H19O	0.9735
Cu2—N2	1.970 (3)	O19—H19P	0.7701
Cu2—Na1	3.3549 (15)	O22—C16	1.425 (6)
Cu3—O3	1.893 (2)	O24—C10	1.451 (5)
Cu3—O7	1.916 (3)	O25—H25O	0.8537
Cu3—O2	1.926 (2)	O25—H25P	0.8473
Cu3—O6	1.967 (2)	O26—H26A	0.8500
Cu3—O4	2.187 (3)	O26—H26B	0.8500
Cu4—O7	1.903 (2)	O27—H27O	0.9116

Cu4—O15	1.905 (2)	O27—H27P	0.9138
Cu4—O8	1.929 (3)	O28—H28O	0.9031
Cu4—N4	1.961 (3)	O28—H28P	0.8226
Cu5—O9	1.942 (2)	O29—C19	1.248 (5)
Cu5—O6	1.949 (2)	O30—C19	1.267 (5)
Cu5—N3	1.952 (3)	O31—H31O	0.9530
Cu5—O10	1.961 (3)	O31—H31P	0.8146
Cu5—O5	2.338 (3)	O32A—H32A	0.8500
Cu5—Na3	3.2854 (19)	O32A—H32B	0.8500
Cu5—Na4	3.3120 (15)	O32B—H32C	0.8499
P1—O14	1.500 (3)	O32B—H32D	0.8499
P1—O12	1.525 (3)	N1—C5	1.300 (5)
P1—O13	1.575 (3)	N2—C1	1.306 (5)
P1—C2	1.802 (4)	N3—C8	1.299 (5)
P2—O17	1.496 (3)	N4—C12	1.298 (5)
P2—O15	1.514 (3)	C1—C2	1.509 (5)
P2—O16	1.584 (3)	C2—H2A	0.9900
P2—C13	1.812 (4)	C2—H2B	0.9900
P3—O23	1.481 (3)	C3A—C4A	1.509 (8)
P3—O10	1.525 (3)	C3A—H3A	0.9900
P3—O24	1.595 (3)	C3A—H3B	0.9900
P3—C9	1.807 (4)	C4A—H4A1	0.9800
P3—Na3	3.208 (2)	C4A—H4A2	0.9800
P4—O20	1.485 (3)	C4A—H4A3	0.9800
P4—O21	1.524 (3)	C3B—C4B	1.73 (2)
P4—O22	1.590 (3)	C3B—H3C	0.9900
P4—C18	1.810 (4)	C3B—H3D	0.9900
Na1—O20	2.259 (3)	C4B—H4B1	0.9800
Na1—O11	2.296 (3)	C4B—H4B2	0.9800

Na1—O19	2.317 (3)	C4B—H4B3	0.9800
Na1—O18	2.318 (3)	C5—C18^{i}	1.501 (5)
Na1—O12	2.663 (3)	C6—C7	1.466 (7)
Na1—Na2	3.323 (2)	C6—H6A	0.9900
Na2—O29^{iii}	2.325 (3)	C6—H6B	0.9900
Na2—O18	2.394 (3)	C7—H7A	0.9800
Na2—O19	2.448 (3)	C7—H7B	0.9800
Na2—O27^{iv}	2.450 (3)	C7—H7C	0.9800
Na2—O29^{iv}	2.468 (3)	C8—C9	1.504 (5)
Na2—O28^{iii}	2.484 (3)	C9—H9A	0.9900
Na2—Na2^{v}	3.475 (3)	C9—H9B	0.9900
Na2—Na4^{iv}	3.581 (2)	C10—C11	1.523 (7)
Na2—Na4^{iii}	3.610 (2)	C10—H10A	0.9900
Na2—H19P	2.5733	C10—H10B	0.9900
Na3—O5	2.220 (4)	C11—H11A	0.9800
Na3—O25	2.244 (4)	C11—H11B	0.9800
Na3—O26	2.283 (4)	C11—H11C	0.9800
Na3—O24	2.479 (3)	C12—C13	1.505 (5)
Na3—O10	2.646 (3)	C13—H13A	0.9900
Na3—O32B	2.68 (2)	C13—H13B	0.9900
Na3—Na4	3.561 (2)	C14—C15	1.535 (7)
Na4—O27	2.350 (3)	C15—H15A	0.9800
Na4—O10	2.369 (3)	C15—H15B	0.9800
Na4—O28	2.399 (3)	C15—H15C	0.9800
Na4—O26	2.448 (4)	C16—C17	1.497 (8)
Na4—O9	2.474 (3)	C16—H16A	0.9900
Na4—O29	2.495 (3)	C16—H16B	0.9900
Na4—H28O	2.5217	C17—H17A	0.9800
O1—C1	1.287 (4)	C17—H17B	0.9800

O2—N2	1.412 (4)	C17—H17C	0.9800
O3—N3	1.403 (4)	C18—H18A	0.9900
O4—C14	1.250 (6)	C18—H18B	0.9900
O5—C14	1.266 (5)	C19—C20	1.497 (5)
O6—N4	1.431 (4)	C20—H20A	0.9800
O7—N1	1.416 (4)	C20—H20B	0.9800
O8—C5	1.301 (4)	C20—H20C	0.9800
O2—Cu1—O21^{i}	170.84 (13)	O10—Na4—Na2^{iii}	101.73 (8)
O2—Cu1—O1	80.75 (10)	O28—Na4—Na2^{iii}	43.24 (7)
O21^{i}—Cu1—O1	95.23 (11)	O26—Na4—Na2^{iii}	129.42 (12)
O2—Cu1—N1	90.00 (11)	O9—Na4—Na2^{iii}	142.74 (9)
O21^{i}—Cu1—N1	93.44 (12)	O29—Na4—Na2^{iii}	39.73 (7)
O1—Cu1—N1	170.17 (12)	Cu5—Na4—Na2^{iii}	122.29 (5)
O2—Cu1—O6^{ii}	98.46 (11)	Na3—Na4—Na2^{iii}	133.93 (6)
O21^{i}—Cu1—O6^{ii}	89.92 (10)	Na2^{vi}—Na4—Na2^{iii}	57.79 (5)
O1—Cu1—O6^{ii}	92.73 (10)	O27—Na4—H28O	82.5
N1—Cu1—O6^{ii}	91.91 (11)	O10—Na4—H28O	100.4
O3—Cu2—O12	172.95 (11)	O28—Na4—H28O	21.0
O3—Cu2—O11	81.62 (10)	O26—Na4—H28O	167.7
O12—Cu2—O11	91.38 (11)	O9—Na4—H28O	85.4
O3—Cu2—N2	89.90 (11)	O29—Na4—H28O	97.4
O12—Cu2—N2	97.11 (12)	Cu5—Na4—H28O	86.8
O11—Cu2—N2	171.40 (11)	Na3—Na4—H28O	143.5
O3—Cu2—Na1	120.58 (8)	Na2^{vi}—Na4—H28O	85.9
O12—Cu2—Na1	52.43 (8)	Na2^{iii}—Na4—H28O	59.6
O11—Cu2—Na1	41.56 (7)	C1—O1—Cu1	110.8 (2)
N2—Cu2—Na1	146.87 (9)	N2—O2—Cu1	113.4 (2)
O3—Cu3—O7	164.08 (12)	N2—O2—Cu3	122.4 (2)
O3—Cu3—O2	87.70 (11)	Cu1—O2—Cu3	119.19 (13)

O7—Cu3—O2	89.54 (10)	N3—O3—Cu2	115.1 (2)
O3—Cu3—O6	92.04 (10)	N3—O3—Cu3	121.2 (2)
O7—Cu3—O6	86.94 (10)	Cu2—O3—Cu3	123.60 (13)
O2—Cu3—O6	166.18 (11)	C14—O4—Cu3	126.7 (3)
O3—Cu3—O4	98.20 (13)	C14—O5—Na3	137.4 (3)
O7—Cu3—O4	97.71 (12)	C14—O5—Cu5	130.1 (3)
O2—Cu3—O4	97.55 (12)	Na3—O5—Cu5	92.22 (12)
O6—Cu3—O4	96.17 (12)	N4—O6—Cu5	108.66 (18)
O7—Cu4—O15	173.60 (11)	N4—O6—Cu3	113.06 (19)
O7—Cu4—O8	81.16 (10)	Cu5—O6—Cu3	107.84 (12)
O15—Cu4—O8	92.45 (11)	N4—O6—Cu1^{ii}	109.94 (18)
O7—Cu4—N4	91.72 (11)	Cu5—O6—Cu1^{ii}	106.93 (11)
O15—Cu4—N4	94.68 (11)	Cu3—O6—Cu1^{ii}	110.18 (10)
O8—Cu4—N4	172.43 (11)	N1—O7—Cu4	112.66 (19)
O9—Cu5—O6	81.70 (10)	N1—O7—Cu3	119.6 (2)
O9—Cu5—N3	174.55 (12)	Cu4—O7—Cu3	114.59 (12)
O6—Cu5—N3	93.14 (11)	C5—O8—Cu4	111.1 (2)
O9—Cu5—O10	91.11 (11)	C12—O9—Cu5	108.9 (2)
O6—Cu5—O10	169.18 (11)	C12—O9—Na4	154.6 (2)
N3—Cu5—O10	94.24 (12)	Cu5—O9—Na4	96.42 (10)
O9—Cu5—O5	86.47 (11)	P3—O10—Cu5	127.92 (16)
O6—Cu5—O5	92.70 (11)	P3—O10—Na4	132.00 (15)
N3—Cu5—O5	92.05 (12)	Cu5—O10—Na4	99.38 (11)
O10—Cu5—O5	94.93 (12)	P3—O10—Na3	96.84 (14)
O9—Cu5—Na3	79.39 (8)	Cu5—O10—Na3	89.71 (11)
O6—Cu5—Na3	131.83 (8)	Na4—O10—Na3	90.31 (10)
N3—Cu5—Na3	103.01 (10)	C8—O11—Cu2	110.5 (2)
O10—Cu5—Na3	53.65 (9)	C8—O11—Na1	139.6 (2)
O5—Cu5—Na3	42.46 (8)	Cu2—O11—Na1	104.21 (11)

O9—Cu5—Na4	47.94 (8)	P1—O12—Cu2	123.96 (16)
O6—Cu5—Na4	125.86 (8)	P1—O12—Na1	142.59 (15)
N3—Cu5—Na4	137.50 (9)	Cu2—O12—Na1	93.14 (10)
O10—Cu5—Na4	44.89 (8)	C3B—O13—P1	131.8 (9)
O5—Cu5—Na4	101.16 (8)	C3A—O13—P1	120.2 (3)
Na3—Cu5—Na4	65.33 (4)	P2—O15—Cu4	121.63 (15)
O14—P1—O12	112.33 (15)	C6—O16—P2	119.9 (3)
O14—P1—O13	110.70 (17)	Na1—O18—Na2	89.67 (11)
O12—P1—O13	110.06 (16)	Na1—O18—H18O	103.5
O14—P1—C2	109.72 (17)	Na2—O18—H18O	131.7
O12—P1—C2	110.97 (17)	Na1—O18—H18P	130.9
O13—P1—C2	102.64 (17)	Na2—O18—H18P	110.0
O17—P2—O15	114.91 (15)	H18O—O18—H18P	95.9
O17—P2—O16	110.95 (16)	Na1—O19—Na2	88.40 (10)
O15—P2—O16	106.12 (16)	Na1—O19—H19O	115.6
O17—P2—C13	109.20 (16)	Na2—O19—H19O	98.2
O15—P2—C13	109.13 (16)	Na1—O19—H19P	148.9
O16—P2—C13	106.14 (18)	Na2—O19—H19P	90.6
O23—P3—O10	117.45 (16)	H19O—O19—H19P	95.3
O23—P3—O24	111.73 (16)	P4—O20—Na1	162.3 (2)
O10—P3—O24	103.11 (15)	P4—O21—Cu1^{vii}	118.67 (15)
O23—P3—C9	108.50 (17)	C16—O22—P4	121.8 (3)
O10—P3—C9	109.33 (17)	C10—O24—P3	122.5 (3)
O24—P3—C9	106.10 (17)	C10—O24—Na3	121.2 (3)
O23—P3—Na3	122.95 (12)	P3—O24—Na3	101.67 (14)
O10—P3—Na3	54.99 (12)	Na3—O25—H25O	133.2
O24—P3—Na3	49.18 (11)	Na3—O25—H25P	116.8
C9—P3—Na3	127.86 (13)	H25O—O25—H25P	108.6
O20—P4—O21	113.23 (16)	Na3—O26—Na4	97.60 (13)

O20—P4—O22	112.61 (19)	Na3—O26—H26A	112.4
O21—P4—O22	109.23 (17)	Na4—O26—H26A	112.4
O20—P4—C18	110.63 (17)	Na3—O26—H26B	112.0
O21—P4—C18	110.78 (17)	Na4—O26—H26B	112.1
O22—P4—C18	99.55 (17)	H26A—O26—H26B	109.8
O20—Na1—O11	101.27 (11)	Na4—O27—Na2^{vi}	96.46 (10)
O20—Na1—O19	116.45 (12)	Na4—O27—H27O	123.2
O11—Na1—O19	136.27 (12)	Na2^{vi}—O27—H27O	117.5
O20—Na1—O18	98.56 (12)	Na4—O27—H27P	108.4
O11—Na1—O18	105.96 (11)	Na2^{vi}—O27—H27P	103.6
O19—Na1—O18	90.18 (11)	H27O—O27—H27P	105.9
O20—Na1—O12	167.88 (11)	Na4—O28—Na2^{iii}	95.32 (10)
O11—Na1—O12	66.95 (9)	Na4—O28—H28O	87.2
O19—Na1—O12	73.53 (9)	Na2^{iii}—O28—H28O	135.5
O18—Na1—O12	87.89 (10)	Na4—O28—H28P	107.7
O20—Na1—Na2	101.10 (9)	Na2^{iii}—O28—H28P	119.4
O11—Na1—Na2	146.59 (9)	H28O—O28—H28P	101.6
O19—Na1—Na2	47.42 (8)	C19—O29—Na2^{iii}	124.6 (3)
O18—Na1—Na2	46.09 (7)	C19—O29—Na2^{vi}	118.1 (2)
O12—Na1—Na2	90.77 (7)	Na2^{iii}—O29—Na2^{vi}	92.88 (10)
O20—Na1—Cu2	134.60 (9)	C19—O29—Na4	123.7 (3)
O11—Na1—Cu2	34.22 (7)	Na2^{iii}—O29—Na4	96.96 (10)
O19—Na1—Cu2	107.85 (8)	Na2^{vi}—O29—Na4	92.35 (10)
O18—Na1—Cu2	90.49 (8)	H31O—O31—H31P	107.9
O12—Na1—Cu2	34.43 (6)	H32A—O32A—H32B	109.7
Na2—Na1—Cu2	116.36 (5)	Na3—O32B—H32C	116.3
O29^{iii}—Na2—O18	100.37 (11)	Na3—O32B—H32D	105.4
O29^{iii}—Na2—O19	167.68 (11)	H32C—O32B—H32D	111.4
O18—Na2—O19	85.35 (10)	C5—N1—O7	110.7 (3)

O29^{iii}—Na2—O27^{iv}	102.46 (11)	C5—N1—Cu1	135.4 (3)
O18—Na2—O27^{iv}	96.60 (10)	O7—N1—Cu1	113.6 (2)
O19—Na2—O27^{iv}	87.56 (10)	C1—N2—O2	110.5 (3)
O29^{iii}—Na2—O29^{iv}	87.12 (10)	C1—N2—Cu2	133.8 (3)
O18—Na2—O29^{iv}	171.95 (11)	O2—N2—Cu2	115.6 (2)
O19—Na2—O29^{iv}	86.73 (10)	C8—N3—O3	110.4 (3)
O27^{iv}—Na2—O29^{iv}	84.52 (10)	C8—N3—Cu5	136.0 (3)
O29^{iii}—Na2—O28^{iii}	84.70 (10)	O3—N3—Cu5	113.3 (2)
O18—Na2—O28^{iii}	87.37 (10)	C12—N4—O6	111.8 (3)
O19—Na2—O28^{iii}	84.68 (10)	C12—N4—Cu4	134.6 (3)
O27^{iv}—Na2—O28^{iii}	170.97 (11)	O6—N4—Cu4	113.5 (2)
O29^{iv}—Na2—O28^{iii}	90.43 (10)	O1—C1—N2	122.2 (3)
O29^{iii}—Na2—Na1	136.54 (9)	O1—C1—C2	117.7 (3)
O18—Na2—Na1	44.24 (8)	N2—C1—C2	120.1 (3)
O19—Na2—Na1	44.18 (7)	C1—C2—P1	119.3 (3)
O27^{iv}—Na2—Na1	105.56 (8)	C1—C2—H2A	107.5
O29^{iv}—Na2—Na1	127.78 (9)	P1—C2—H2A	107.5
O28^{iii}—Na2—Na1	71.76 (7)	C1—C2—H2B	107.5
O29^{iii}—Na2—Na2^{v}	45.20 (7)	P1—C2—H2B	107.5
O18—Na2—Na2^{v}	145.47 (11)	H2A—C2—H2B	107.0
O19—Na2—Na2^{v}	127.82 (10)	O13—C3A—C4A	109.2 (5)
O27^{iv}—Na2—Na2^{v}	94.39 (8)	O13—C3A—H3A	109.8
O29^{iv}—Na2—Na2^{v}	41.93 (7)	C4A—C3A—H3A	109.8
O28^{iii}—Na2—Na2^{v}	86.77 (8)	O13—C3A—H3B	109.8
Na1—Na2—Na2^{v}	157.05 (8)	C4A—C3A—H3B	109.8
O29^{iii}—Na2—Na4^{iv}	92.86 (8)	H3A—C3A—H3B	108.3
O18—Na2—Na4^{iv}	137.28 (9)	C3A—C4A—H4A1	109.5
O19—Na2—Na4^{iv}	90.14 (8)	C3A—C4A—H4A2	109.5
O27^{iv}—Na2—Na4^{iv}	40.71 (7)	H4A1—C4A—H4A2	109.5

O29^{iv}—Na2—Na4^{iv}	44.11 (7)	C3A—C4A—H4A3	109.5
O28^{iii}—Na2—Na4^{iv}	134.52 (8)	H4A1—C4A—H4A3	109.5
Na1—Na2—Na4^{iv}	129.70 (6)	H4A2—C4A—H4A3	109.5
Na2^{v}—Na2—Na4^{iv}	61.53 (5)	O13—C3B—C4B	103.0 (12)
O29^{iii}—Na2—Na4^{iii}	43.31 (7)	O13—C3B—H3C	111.2
O18—Na2—Na4^{iii}	93.68 (8)	C4B—C3B—H3C	111.2
O19—Na2—Na4^{iii}	125.99 (8)	O13—C3B—H3D	111.2
O27^{iv}—Na2—Na4^{iii}	145.64 (9)	C4B—C3B—H3D	111.2
O29^{iv}—Na2—Na4^{iii}	89.77 (8)	H3C—C3B—H3D	109.1
O28^{iii}—Na2—Na4^{iii}	41.43 (7)	C3B—C4B—H4B1	109.5
Na1—Na2—Na4^{iii}	104.64 (5)	C3B—C4B—H4B2	109.5
Na2^{v}—Na2—Na4^{iii}	60.68 (5)	H4B1—C4B—H4B2	109.5
Na4^{iv}—Na2—Na4^{iii}	122.21 (5)	C3B—C4B—H4B3	109.5
O29^{iii}—Na2—H19P	152.9	H4B1—C4B—H4B3	109.5
O18—Na2—H19P	102.4	H4B2—C4B—H4B3	109.5
O19—Na2—H19P	17.4	N1—C5—O8	121.6 (3)
O27^{iv}—Na2—H19P	89.4	N1—C5—C18^{i}	121.1 (3)
O29^{iv}—Na2—H19P	69.7	O8—C5—C18^{i}	117.3 (3)
O28^{iii}—Na2—H19P	81.9	O16—C6—C7	110.2 (4)
Na1—Na2—H19P	59.6	O16—C6—H6A	109.6
Na2^{v}—Na2—H19P	110.4	C7—C6—H6A	109.6
Na4^{iv}—Na2—H19P	80.3	O16—C6—H6B	109.6
Na4^{iii}—Na2—H19P	120.2	C7—C6—H6B	109.6
O5—Na3—O25	112.75 (14)	H6A—C6—H6B	108.1
O5—Na3—O26	120.16 (16)	C6—C7—H7A	109.5
O25—Na3—O26	110.65 (15)	C6—C7—H7B	109.5
O5—Na3—O24	100.55 (12)	H7A—C7—H7B	109.5
O25—Na3—O24	91.29 (14)	C6—C7—H7C	109.5
O26—Na3—O24	117.60 (15)	H7A—C7—H7C	109.5

O5—Na3—O10	81.03 (11)	H7B—C7—H7C	109.5
O25—Na3—O10	147.77 (14)	O11—C8—N3	122.3 (3)
O26—Na3—O10	83.55 (12)	O11—C8—C9	119.1 (3)
O24—Na3—O10	56.87 (9)	N3—C8—C9	118.5 (3)
O5—Na3—O32B	174.9 (4)	C8—C9—P3	117.8 (3)
O25—Na3—O32B	72.1 (4)	C8—C9—H9A	107.9
O26—Na3—O32B	55.4 (4)	P3—C9—H9A	107.9
O24—Na3—O32B	80.5 (5)	C8—C9—H9B	107.9
O10—Na3—O32B	95.5 (5)	P3—C9—H9B	107.9
O5—Na3—P3	94.23 (10)	H9A—C9—H9B	107.2
O25—Na3—P3	119.61 (12)	O24—C10—C11	111.2 (4)
O26—Na3—P3	98.24 (11)	O24—C10—H10A	109.4
O24—Na3—P3	29.15 (7)	C11—C10—H10A	109.4
O10—Na3—P3	28.17 (6)	O24—C10—H10B	109.4
O32B—Na3—P3	84.3 (5)	C11—C10—H10B	109.4
O5—Na3—Cu5	45.32 (9)	H10A—C10—H10B	108.0
O25—Na3—Cu5	152.16 (12)	C10—C11—H11A	109.5
O26—Na3—Cu5	96.86 (11)	C10—C11—H11B	109.5
O24—Na3—Cu5	79.21 (8)	H11A—C11—H11B	109.5
O10—Na3—Cu5	36.64 (6)	C10—C11—H11C	109.5
O32B—Na3—Cu5	130.6 (4)	H11A—C11—H11C	109.5
P3—Na3—Cu5	57.78 (4)	H11B—C11—H11C	109.5
O5—Na3—Na4	96.63 (10)	N4—C12—O9	122.7 (3)
O25—Na3—Na4	149.50 (12)	N4—C12—C13	120.5 (3)
O26—Na3—Na4	42.95 (9)	O9—C12—C13	116.7 (3)
O24—Na3—Na4	91.22 (9)	C12—C13—P2	119.4 (3)
O10—Na3—Na4	41.70 (6)	C12—C13—H13A	107.5
O32B—Na3—Na4	78.3 (4)	P2—C13—H13A	107.5
P3—Na3—Na4	63.49 (4)	C12—C13—H13B	107.5

Cu5—Na3—Na4	57.70 (4)	P2—C13—H13B	107.5
O27—Na4—O10	164.64 (12)	H13A—C13—H13B	107.0
O27—Na4—O28	96.48 (11)	O4—C14—O5	126.0 (4)
O10—Na4—O28	90.75 (11)	O4—C14—C15	117.4 (4)
O27—Na4—O26	88.39 (11)	O5—C14—C15	116.5 (4)
O10—Na4—O26	86.31 (11)	C14—C15—H15A	109.5
O28—Na4—O26	171.19 (14)	C14—C15—H15B	109.5
O27—Na4—O9	95.16 (10)	H15A—C15—H15B	109.5
O10—Na4—O9	70.20 (9)	C14—C15—H15C	109.5
O28—Na4—O9	99.61 (10)	H15A—C15—H15C	109.5
O26—Na4—O9	87.21 (13)	H15B—C15—H15C	109.5
O27—Na4—O29	86.04 (10)	O22—C16—C17	110.1 (4)
O10—Na4—O29	108.36 (10)	O22—C16—H16A	109.6
O28—Na4—O29	82.94 (10)	C17—C16—H16A	109.6
O26—Na4—O29	90.10 (13)	O22—C16—H16B	109.6
O9—Na4—O29	177.02 (11)	C17—C16—H16B	109.6
O27—Na4—Cu5	130.46 (9)	H16A—C16—H16B	108.2
O10—Na4—Cu5	35.74 (7)	C16—C17—H17A	109.5
O28—Na4—Cu5	89.46 (8)	C16—C17—H17B	109.5
O26—Na4—Cu5	92.96 (10)	H17A—C17—H17B	109.5
O9—Na4—Cu5	35.64 (6)	C16—C17—H17C	109.5
O29—Na4—Cu5	143.41 (8)	H17A—C17—H17C	109.5
O27—Na4—Na3	123.06 (9)	H17B—C17—H17C	109.5
O10—Na4—Na3	47.99 (8)	C5^{vii}—C18—P4	118.8 (3)
O28—Na4—Na3	138.69 (9)	C5^{vii}—C18—H18A	107.6
O26—Na4—Na3	39.45 (9)	P4—C18—H18A	107.6
O9—Na4—Na3	68.05 (8)	C5^{vii}—C18—H18B	107.6
O29—Na4—Na3	109.02 (8)	P4—C18—H18B	107.6
Cu5—Na4—Na3	56.97 (4)	H18A—C18—H18B	107.1

O27—Na4—Na2^{vi}	42.83 (7)	O29—C19—O30	123.0 (4)
O10—Na4—Na2^{vi}	151.88 (9)	O29—C19—C20	120.9 (4)
O28—Na4—Na2^{vi}	85.63 (8)	O30—C19—C20	116.1 (4)
O26—Na4—Na2^{vi}	93.05 (10)	C19—C20—H20A	109.5
O9—Na4—Na2^{vi}	137.89 (8)	C19—C20—H20B	109.5
O29—Na4—Na2^{vi}	43.53 (7)	H20A—C20—H20B	109.5
Cu5—Na4—Na2^{vi}	170.79 (6)	C19—C20—H20C	109.5
Na3—Na4—Na2^{vi}	130.66 (6)	H20A—C20—H20C	109.5
O27—Na4—Na2^{iii}	92.77 (8)	H20B—C20—H20C	109.5
O11—Cu2—O3—N3	2.0 (2)	Cu2—O3—N3—Cu5	−177.40 (14)
N2—Cu2—O3—N3	−179.4 (2)	Cu3—O3—N3—Cu5	5.5 (3)
Na1—Cu2—O3—N3	−13.0 (3)	Cu5—O6—N4—C12	19.6 (3)
O11—Cu2—O3—Cu3	179.03 (19)	Cu3—O6—N4—C12	139.3 (3)
N2—Cu2—O3—Cu3	−2.40 (19)	Cu1^{ii}—O6—N4—C12	−97.1 (3)
Na1—Cu2—O3—Cu3	163.94 (12)	Cu5—O6—N4—Cu4	−158.20 (14)
O7—Cu3—O3—N3	102.6 (4)	Cu3—O6—N4—Cu4	−38.5 (3)
O2—Cu3—O3—N3	−177.2 (3)	Cu1^{ii}—O6—N4—Cu4	85.1 (2)
O6—Cu3—O3—N3	16.6 (3)	Cu1—O1—C1—N2	8.7 (4)
O4—Cu3—O3—N3	−80.0 (3)	Cu1—O1—C1—C2	−169.1 (3)
O7—Cu3—O3—Cu2	−74.2 (4)	O2—N2—C1—O1	2.5 (5)
O2—Cu3—O3—Cu2	5.95 (18)	Cu2—N2—C1—O1	−174.1 (3)
O6—Cu3—O3—Cu2	−160.22 (18)	O2—N2—C1—C2	−179.8 (3)
O4—Cu3—O3—Cu2	103.25 (18)	Cu2—N2—C1—C2	3.6 (6)
O23—P3—O10—Cu5	152.40 (19)	O1—C1—C2—P1	−160.1 (3)
O24—P3—O10—Cu5	−84.3 (2)	N2—C1—C2—P1	22.1 (5)
C9—P3—O10—Cu5	28.3 (3)	O14—P1—C2—C1	−168.6 (3)
Na3—P3—O10—Cu5	−95.0 (2)	O12—P1—C2—C1	−43.9 (4)
O23—P3—O10—Na4	−16.0 (3)	O13—P1—C2—C1	73.7 (3)
O24—P3—O10—Na4	107.3 (2)	P1—O13—C3A—C4A	−179.9 (4)

C9—P3—O10—Na4	−140.1 (2)	P1—O13—C3B—C4B	−148.0 (6)
Na3—P3—O10—Na4	96.6 (2)	O7—N1—C5—O8	−2.7 (5)
O23—P3—O10—Na3	−112.61 (16)	Cu1—N1—C5—O8	−175.3 (3)
O24—P3—O10—Na3	10.71 (15)	O7—N1—C5—C18^{i}	178.5 (3)
C9—P3—O10—Na3	123.25 (16)	Cu1—N1—C5—C18^{i}	5.8 (6)
O14—P1—O12—Cu2	164.42 (18)	Cu4—O8—C5—N1	−9.6 (4)
O13—P1—O12—Cu2	−71.7 (2)	Cu4—O8—C5—C18^{i}	169.2 (3)
C2—P1—O12—Cu2	41.2 (3)	P2—O16—C6—C7	160.6 (4)
O14—P1—O12—Na1	−24.1 (3)	Cu2—O11—C8—N3	0.3 (4)
O13—P1—O12—Na1	99.8 (3)	Na1—O11—C8—N3	147.8 (3)
C2—P1—O12—Na1	−147.3 (2)	Cu2—O11—C8—C9	−176.7 (3)
O11—Cu2—O12—P1	159.2 (2)	Na1—O11—C8—C9	−29.1 (6)
N2—Cu2—O12—P1	−19.5 (2)	O3—N3—C8—O11	1.4 (5)
Na1—Cu2—O12—P1	174.8 (3)	Cu5—N3—C8—O11	174.7 (3)
O11—Cu2—O12—Na1	−15.67 (11)	O3—N3—C8—C9	178.3 (3)
N2—Cu2—O12—Na1	165.64 (12)	Cu5—N3—C8—C9	−8.3 (6)
O14—P1—O13—C3B	136.6 (12)	O11—C8—C9—P3	−143.8 (3)
O12—P1—O13—C3B	11.8 (12)	N3—C8—C9—P3	39.2 (5)
C2—P1—O13—C3B	−106.4 (12)	O23—P3—C9—C8	−177.1 (3)
O14—P1—O13—C3A	65.7 (4)	O10—P3—C9—C8	−47.8 (4)
O12—P1—O13—C3A	−59.1 (4)	O24—P3—C9—C8	62.7 (3)
C2—P1—O13—C3A	−177.2 (4)	Na3—P3—C9—C8	12.3 (4)
O17—P2—O15—Cu4	176.00 (16)	P3—O24—C10—C11	−85.4 (5)
O16—P2—O15—Cu4	−61.0 (2)	Na3—O24—C10—C11	142.9 (4)
C13—P2—O15—Cu4	53.0 (2)	O6—N4—C12—O9	−3.1 (5)
O17—P2—O16—C6	−35.9 (4)	Cu4—N4—C12—O9	174.1 (3)
O15—P2—O16—C6	−161.4 (4)	O6—N4—C12—C13	175.4 (3)
C13—P2—O16—C6	82.6 (4)	Cu4—N4—C12—C13	−7.4 (6)
O21—P4—O20—Na1	111.9 (6)	Cu5—O9—C12—N4	−15.2 (4)

O22—P4—O20—Na1	−12.6 (7)	Na4—O9—C12—N4	160.9 (4)
C18—P4—O20—Na1	−123.1 (6)	Cu5—O9—C12—C13	166.2 (3)
O20—P4—O21—Cu1^{vii}	−178.40 (18)	Na4—O9—C12—C13	−17.6 (8)
O22—P4—O21—Cu1^{vii}	−52.0 (2)	N4—C12—C13—P2	18.5 (5)
C18—P4—O21—Cu1^{vii}	56.6 (2)	O9—C12—C13—P2	−162.9 (3)
O20—P4—O22—C16	78.7 (4)	O17—P2—C13—C12	−167.3 (3)
O21—P4—O22—C16	−48.0 (4)	O15—P2—C13—C12	−40.9 (4)
C18—P4—O22—C16	−164.1 (4)	O16—P2—C13—C12	73.1 (3)
O23—P3—O24—C10	−23.9 (4)	Cu3—O4—C14—O5	9.0 (7)
O10—P3—O24—C10	−150.9 (3)	Cu3—O4—C14—C15	−173.4 (3)
C9—P3—O24—C10	94.2 (3)	Na3—O5—C14—O4	−171.5 (3)
Na3—P3—O24—C10	−139.3 (4)	Cu5—O5—C14—O4	0.9 (7)
O23—P3—O24—Na3	115.44 (15)	Na3—O5—C14—C15	10.9 (7)
O10—P3—O24—Na3	−11.60 (16)	Cu5—O5—C14—C15	−176.7 (3)
C9—P3—O24—Na3	−126.49 (15)	P4—O22—C16—C17	178.8 (4)
Cu4—O7—N1—C5	14.0 (4)	O20—P4—C18—C5^{vii}	−161.6 (3)
Cu3—O7—N1—C5	153.1 (2)	O21—P4—C18—C5^{vii}	−35.2 (3)
Cu4—O7—N1—Cu1	−171.64 (13)	O22—P4—C18—C5^{vii}	79.7 (3)
Cu3—O7—N1—Cu1	−32.6 (3)	Na2^{iii}—O29—C19—O30	164.4 (3)
Cu1—O2—N2—C1	−12.9 (4)	Na2^{vi}—O29—C19—O30	48.4 (5)
Cu3—O2—N2—C1	−167.5 (2)	Na4—O29—C19—O30	−66.0 (5)
Cu1—O2—N2—Cu2	164.40 (15)	Na2^{iii}—O29—C19—C20	−15.3 (5)
Cu3—O2—N2—Cu2	9.8 (3)	Na2^{vi}—O29—C19—C20	−131.3 (3)
Cu2—O3—N3—C8	−2.4 (4)	Na4—O29—C19—C20	114.3 (4)
Cu3—O3—N3—C8	−179.5 (2)		

Symmetry codes: (i) *x*, *y*−1, *z*; (ii) −*x*, −*y*+1, −*z*+2; (iii) −*x*, −*y*+2, −*z*+2; (iv) *x*, *y*, *z*−1; (v) −*x*, −*y*+2, −*z*+1; (vi) *x*, *y*, *z*+1; (vii) *x*, *y*+1, *z*.

Table S5. Selected bond distances (Å) and angles (°) for **1**.

Cu1—O2	1.901 (3)
Cu1—O21^{i}	1.926 (3)
Cu1—O1	1.955 (3)
Cu1—N1	1.971 (3)
Cu1—O6^{ii}	2.439 (3)
Cu2—O3	1.864 (2)
Cu2—O12	1.900 (3)
Cu2—O11	1.947 (2)
Cu2—N2	1.970 (3)
Cu2—Na1	3.3549 (15)
Cu3—O3	1.893 (2)
Cu3—O7	1.916 (3)
Cu3—O2	1.926 (2)
Cu3—O6	1.967 (2)
Cu3—O4	2.187 (3)
Cu4—O7	1.903 (2)
Cu4—O15	1.905 (2)
Cu4—O8	1.929 (3)
Cu4—N4	1.961 (3)
Cu5—O9	1.942 (2)
Cu5—O6	1.949 (2)
Cu5—N3	1.952 (3)
Cu5—O10	1.961 (3)
Cu5—O5	2.338 (3)
O2—Cu1—O21^{i}	170.84 (13)
O2—Cu1—O1	80.75 (10)
O21^{i}—Cu1—O1	95.23 (11)

O2—Cu1—N1	90.00 (11)
O21^{i}—Cu1—N1	93.44 (12)
O1—Cu1—N1	170.17 (12)
O2—Cu1—O6^{ii}	98.46 (11)
O21^{i}—Cu1—O6^{ii}	89.92 (10)
O1—Cu1—O6^{ii}	92.73 (10)
N1—Cu1—O6^{ii}	91.91 (11)
O3—Cu2—O12	172.95 (11)
O3—Cu2—O11	81.62 (10)
O12—Cu2—O11	91.38 (11)
O3—Cu2—N2	89.90 (11)
O12—Cu2—N2	97.11 (12)
O11—Cu2—N2	171.40 (11)
O3—Cu2—Na1	120.58 (8)
O12—Cu2—Na1	52.43 (8)
O11—Cu2—Na1	41.56 (7)
N2—Cu2—Na1	146.87 (9)
O3—Cu3—O7	164.08 (12)
O3—Cu3—O2	87.70 (11)
O7—Cu3—O2	89.54 (10)
O3—Cu3—O6	92.04 (10)
O7—Cu3—O6	86.94 (10)
O2—Cu3—O6	166.18 (11)
O3—Cu3—O4	98.20 (13)
O7—Cu3—O4	97.71 (12)
O2—Cu3—O4	97.55 (12)
O6—Cu3—O4	96.17 (12)
O7—Cu4—O15	173.60 (11)

O7—Cu4—O8	81.16 (10)
O15—Cu4—O8	92.45 (11)
O7—Cu4—N4	91.72 (11)
O15—Cu4—N4	94.68 (11)
O8—Cu4—N4	172.43 (11)
O9—Cu5—O6	81.70 (10)
O9—Cu5—N3	174.55 (12)
O6—Cu5—N3	93.14 (11)
O9—Cu5—O10	91.11 (11)
O6—Cu5—O10	169.18 (11)
N3—Cu5—O10	94.24 (12)

Symmetry codes: (i) *x*, *y*−1, *z*; (ii) −*x*, −*y*+1, −*z*+2.

Table S6. Hydrogen bonding details of **1** (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O18—H18*O*···O8^{ii}	0.95	1.98	2.875 (4)	156
O18—H18*P*···O23^{iii}	0.94	1.78	2.722 (4)	176
O19—H19*O*···O14	0.97	1.98	2.940 (4)	168
O25—H25*O*···O31^{viii}	0.85	1.99	2.803 (4)	159
O25—H25*P*···O30^{ix}	0.85	1.98	2.825 (6)	175
O26—H26*B*···O14^{vi}	0.85	2.11	2.783 (4)	136
O27—H27*O*···O17^{x}	0.91	1.98	2.849 (4)	159
O27—H27*P*···O14^{vi}	0.91	1.89	2.781 (4)	166
O28—H28*P*···O20^{iii}	0.82	2.29	3.038 (4)	151
O28—H28*P*···O21^{iii}	0.82	2.54	3.202 (4)	138
O31—H31*O*···O1	0.95	1.89	2.806 (4)	162
O31—H31*P*···O17^{iv}	0.81	1.94	2.744 (4)	167
O32*A*^{a}—H32*A*^{a}···O30	0.85	1.84	2.524 (11)	136
O32*A*^{a}—H32*A*^{a}···O32*A*^{a}ix	0.85	2.19	2.68 (2)	116

O32*A*a—H32*B*$^{a\cdots O30}$ix	0.85	2.07	2.884 (11)	161
O32*B*b—H32*D*$^{b\cdots O30}$ix	0.85	2.19	2.684 (19)	117
O32*B*b—H32*C*$^{b\cdots O30}$	0.85	1.81	2.63 (2)	164
C2—H2*A*···O15ii	0.99	2.54	3.341 (5)	138
C13—H13*A*···O17x	0.99	2.31	3.253 (5)	159
C20—H20*A*···O23	0.98	2.51	3.259 (5)	133

Symmetry codes: (ii) −*x*, −*y*+1, −*z*+2; (iii) −*x*, −*y*+2, −*z*+2; (iv) *x*, *y*, *z*−1; (vi) *x*, *y*, *z*+1; (viii) −*x*+1, −*y*+1, −*z*+2; (ix) −*x*+1, −*y*+2, −*z*+3; (x) −*x*, −*y*+1, −*z*+3.

Table S7. Crystal data and structure refinement parameters for the X-ray structures of **2**.

Crystal data

$C_{14}H_{16}CuN_3O_5P\cdot1.86(H_2O)$	
M_r = 434.32	D_x = 1.723 Mg m^{-3}
Monoclinic, $P2_1/c$	Melting point: ? K
Hall symbol: ?	Mo $K\alpha$ radiation, λ = 0.71073 Å
a = 9.7384 (2) Å	Cell parameters from 6923 reflections
b = 12.0645 (2) Å	θ = 1.0–27.5°
c = 14.2492 (3) Å	μ = 1.44 mm^{-1}
β = 90.418 (1)°	*T* = 100 K
V = 1674.08 (6) Å^3	Block, bluish green
Z = 4	0.21 × 0.13 × 0.07 mm
F(000) = 894.4	

Data collection

Nonius Kappa CCD diffractometer	3845 independent reflections
	3316 reflections with $I > 2\sigma(I)$
	R_{int} = 0.043

Detector resolution: 9 pixels mm^{-1}	θ_{max} = 27.5°, θ_{min} = 2.2°
φ scans and ω scans with κ offset	*h* = −12 12
Absorption correction: multi-scan SADABS v.2.10 (Sheldrick, 2003)	*k* = −15 15
T_{min} = 0.747, T_{max} = 0.903	*l* = −18 18
36861measured reflections	

Refinement

Refinement on F^2	
Least-squares matrix: full	Hydrogen site location: mixed
$R[F^2 > 2\sigma(F^2)]$ = 0.026	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2)$ = 0.065	$w = 1/[\sigma^2(F_o^2) + (0.0238P)^2 + 1.8596P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.06	$(\Delta/\sigma)_{max}$ = 0.001
3845 reflections	$\Delta\rho_{max}$ = 0.39 e $Å^{-3}$
251 parameters	$\Delta\rho_{min}$ = −0.37 e $Å^{-3}$
0 restraints	Extinction correction: none

Table S8. Bond lengths (Å) and angles (°) for **2**.

Cu1—O3	1.9040 (13)	C4—C5	1.388 (3)
Cu1—O2	1.9627 (13)	C4—H4	0.9500
Cu1—N2	1.9813 (15)	C5—C6	1.482 (3)
Cu1—N1	1.9891 (15)	C6—C7	1.388 (3)
Cu1—O1	2.4159 (13)	C7—C8	1.386 (3)
Cu1—$Cu1^{i}$	6.9971 (2)	C7—H7	0.9500
P1—O4	1.5015 (13)	C8—C9	1.387 (3)
P1—$O1^{ii}$	1.5017 (13)	C8—H8	0.9500
P1—O5	1.5983 (13)	C9—C10	1.389 (3)

P1—C12	1.8252 (19)	C9—H9	0.9500
O2—C11	1.291 (2)	C10—H10	0.9500
O3—N3	1.3728 (19)	C11—C12	1.495 (2)
O5—C13B	1.455 (2)	C12—H12A	0.9900
O5—C13A	1.455 (2)	C12—H12B	0.9900
O7—H7O	0.8202	C13A—C14A	1.490 (3)
O7—H7P	0.8527	C13A—H13A	0.9900
N1—C1	1.342 (2)	C13A—H13B	0.9900
N1—C5	1.356 (2)	C14A—H14A	0.9800
N2—C10	1.338 (2)	C14A—H14B	0.9800
N2—C6	1.353 (2)	C14A—H14C	0.9800
N3—C11	1.298 (2)	O6—H6O	0.9915
N3—H3N	0.87 (2)	O6—H6P	0.9504
C1—C2	1.385 (3)	C13B—C14B	1.580 (17)
C1—H1	0.9500	C13B—H13C	0.9900
C2—C3	1.385 (3)	C13B—H13D	0.9900
C2—H2	0.9500	C14B—H14D	0.9800
C3—C4	1.387 (3)	C14B—H14E	0.9800
C3—H3	0.9500	C14B—H14F	0.9800
O3—Cu1—O2	84.88 (5)	C4—C5—C6	123.67 (17)
O3—Cu1—N2	92.87 (6)	N2—C6—C7	121.41 (17)
O2—Cu1—N2	171.77 (6)	N2—C6—C5	114.45 (16)
O3—Cu1—N1	163.35 (6)	C7—C6—C5	124.13 (16)
O2—Cu1—N1	97.82 (6)	C8—C7—C6	118.72 (17)
N2—Cu1—N1	82.12 (6)	C8—C7—H7	120.6
O3—Cu1—O1	105.02 (5)	C6—C7—H7	120.6
O2—Cu1—O1	99.46 (5)	C7—C8—C9	119.70 (18)
N2—Cu1—O1	88.77 (5)	C7—C8—H8	120.1

N1—Cu1—O1	90.81 (5)	C9—C8—H8	120.1
O3—Cu1—Cu1^{i}	83.93 (4)	C8—C9—C10	118.63 (18)
O2—Cu1—Cu1^{i}	73.62 (4)	C8—C9—H9	120.7
N2—Cu1—Cu1^{i}	114.08 (4)	C10—C9—H9	120.7
N1—Cu1—Cu1^{i}	112.63 (4)	N2—C10—C9	121.78 (17)
O1—Cu1—Cu1^{i}	32.10 (3)	N2—C10—H10	119.1
O4—P1—O1^{ii}	118.93 (7)	C9—C10—H10	119.1
O4—P1—O5	110.21 (7)	O2—C11—N3	119.58 (16)
O1^{ii}—P1—O5	106.07 (7)	O2—C11—C12	122.48 (16)
O4—P1—C12	105.62 (8)	N3—C11—C12	117.90 (16)
O1^{ii}—P1—C12	110.02 (8)	C11—C12—P1	117.54 (13)
O5—P1—C12	105.24 (8)	C11—C12—H12A	107.9
P1^{i}—O1—Cu1	125.77 (7)	P1—C12—H12A	107.9
C11—O2—Cu1	108.63 (11)	C11—C12—H12B	107.9
N3—O3—Cu1	107.53 (10)	P1—C12—H12B	107.9
C13B—O5—P1	118.92 (11)	H12A—C12—H12B	107.2
C13A—O5—P1	118.92 (11)	O5—C13A—C14A	109.23 (17)
H7O—O7—H7P	106.9	O5—C13A—H13A	109.8
C1—N1—C5	119.24 (16)	C14A—C13A—H13A	109.8
C1—N1—Cu1	126.58 (13)	O5—C13A—H13B	109.8
C5—N1—Cu1	114.13 (12)	C14A—C13A—H13B	109.8
C10—N2—C6	119.73 (16)	H13A—C13A—H13B	108.3
C10—N2—Cu1	125.44 (12)	C13A—C14A—H14A	109.5
C6—N2—Cu1	114.54 (12)	C13A—C14A—H14B	109.5
C11—N3—O3	119.35 (15)	H14A—C14A—H14B	109.5
C11—N3—H3N	123.5 (16)	C13A—C14A—H14C	109.5
O3—N3—H3N	117.2 (16)	H14A—C14A—H14C	109.5
N1—C1—C2	121.69 (17)	H14B—C14A—H14C	109.5

N1—C1—H1	119.2	H6O—O6—H6P	103.0
C2—C1—H1	119.2	O5—C13B—C14B	103.1 (7)
C1—C2—C3	119.36 (18)	O5—C13B—H13C	111.1
C1—C2—H2	120.3	C14B—C13B—H13C	111.1
C3—C2—H2	120.3	O5—C13B—H13D	111.1
C2—C3—C4	119.21 (17)	C14B—C13B—H13D	111.1
C2—C3—H3	120.4	H13C—C13B—H13D	109.1
C4—C3—H3	120.4	C13B—C14B—H14D	109.5
C3—C4—C5	118.75 (17)	C13B—C14B—H14E	109.5
C3—C4—H4	120.6	H14D—C14B—H14E	109.5
C5—C4—H4	120.6	C13B—C14B—H14F	109.5
N1—C5—C4	121.73 (17)	H14D—C14B—H14F	109.5
N1—C5—C6	114.60 (16)	H14E—C14B—H14F	109.5
O4—P1—O5—C13B	−38.13 (15)	N1—C5—C6—N2	−4.1 (2)
O1^{ii}—P1—O5—C13B	−168.11 (13)	C4—C5—C6—N2	176.08 (16)
C12—P1—O5—C13B	75.30 (14)	N1—C5—C6—C7	175.05 (17)
O4—P1—O5—C13A	−38.13 (15)	C4—C5—C6—C7	−4.8 (3)
O1^{ii}—P1—O5—C13A	−168.11 (13)	N2—C6—C7—C8	2.0 (3)
C12—P1—O5—C13A	75.30 (14)	C5—C6—C7—C8	−177.10 (17)
Cu1—O3—N3—C11	1.55 (18)	C6—C7—C8—C9	−2.0 (3)
C5—N1—C1—C2	0.2 (3)	C7—C8—C9—C10	0.6 (3)
Cu1—N1—C1—C2	177.53 (13)	C6—N2—C10—C9	−0.9 (3)
N1—C1—C2—C3	0.5 (3)	Cu1—N2—C10—C9	172.60 (14)
C1—C2—C3—C4	−0.6 (3)	C8—C9—C10—N2	0.9 (3)
C2—C3—C4—C5	0.0 (3)	Cu1—O2—C11—N3	−0.7 (2)
C1—N1—C5—C4	−0.7 (3)	Cu1—O2—C11—C12	−178.21 (13)
Cu1—N1—C5—C4	−178.40 (13)	O3—N3—C11—O2	−0.6 (2)
C1—N1—C5—C6	179.44 (15)	O3—N3—C11—C12	177.03 (14)

Cu1—N1—C5—C6	1.77 (19)	O2—C11—C12—P1	−79.3 (2)
C3—C4—C5—N1	0.6 (3)	N3—C11—C12—P1	103.16 (17)
C3—C4—C5—C6	−179.56 (17)	O4—P1—C12—C11	−167.45 (13)
C10—N2—C6—C7	−0.5 (3)	O1^{ii}—P1—C12—C11	−37.93 (16)
Cu1—N2—C6—C7	−174.75 (14)	O5—P1—C12—C11	75.93 (15)
C10—N2—C6—C5	178.64 (16)	P1—O5—C13A—C14A	−174.01 (15)
Cu1—N2—C6—C5	4.42 (19)	P1—O5—C13B—C14B	−134.1 (9)
Symmetry codes: (i) −*x*, *y*−1/2, −*z*+1/2; (ii) −*x*, *y*+1/2, −*z*+1/2.			

Table S9. Selected bond distances (Å) and angles (°) for **2**.

Cu1—O3	1.9040 (13)
Cu1—O2	1.9627 (13)
Cu1—N2	1.9813 (15)
Cu1—N1	1.9891 (15)
Cu1—O1	2.4159 (13)

O3—Cu1—O2	84.88 (5)
O3—Cu1—N2	92.87 (6)
O2—Cu1—N2	171.77 (6)
O3—Cu1—N1	163.35 (6)
O2—Cu1—N1	97.82 (6)
N2—Cu1—N1	82.12 (6)
O3—Cu1—O1	105.02 (5)
O2—Cu1—O1	99.46 (5)
N2—Cu1—O1	88.77 (5)
N1—Cu1—O1	90.81 (5)

Table S10. Hydrogen bonding details of **2**(Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O6—H6*O*···O2	0.99	1.96	2.901 (2)	159
O6—H6*P*···O7	0.95	1.79	2.729 (2)	168
O7—H7*O*···O1	0.82	2.00	2.8113 (19)	169
O7—H7*P*···O4^{iii}	0.85	1.98	2.8178 (19)	168
N3—H3*N*···O4^{iv}	0.87 (2)	1.91 (3)	2.781 (2)	172 (2)
Symmetry codes: (iii) *x*, −*y*+1/2, *z*+1/2; (iv) −*x*, −*y*, −*z*.				