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SUPPORTING INFORMATION

Title: Synthesis and Coordination Behavior of Symmetrical Tetraamine Phosphinic Acids
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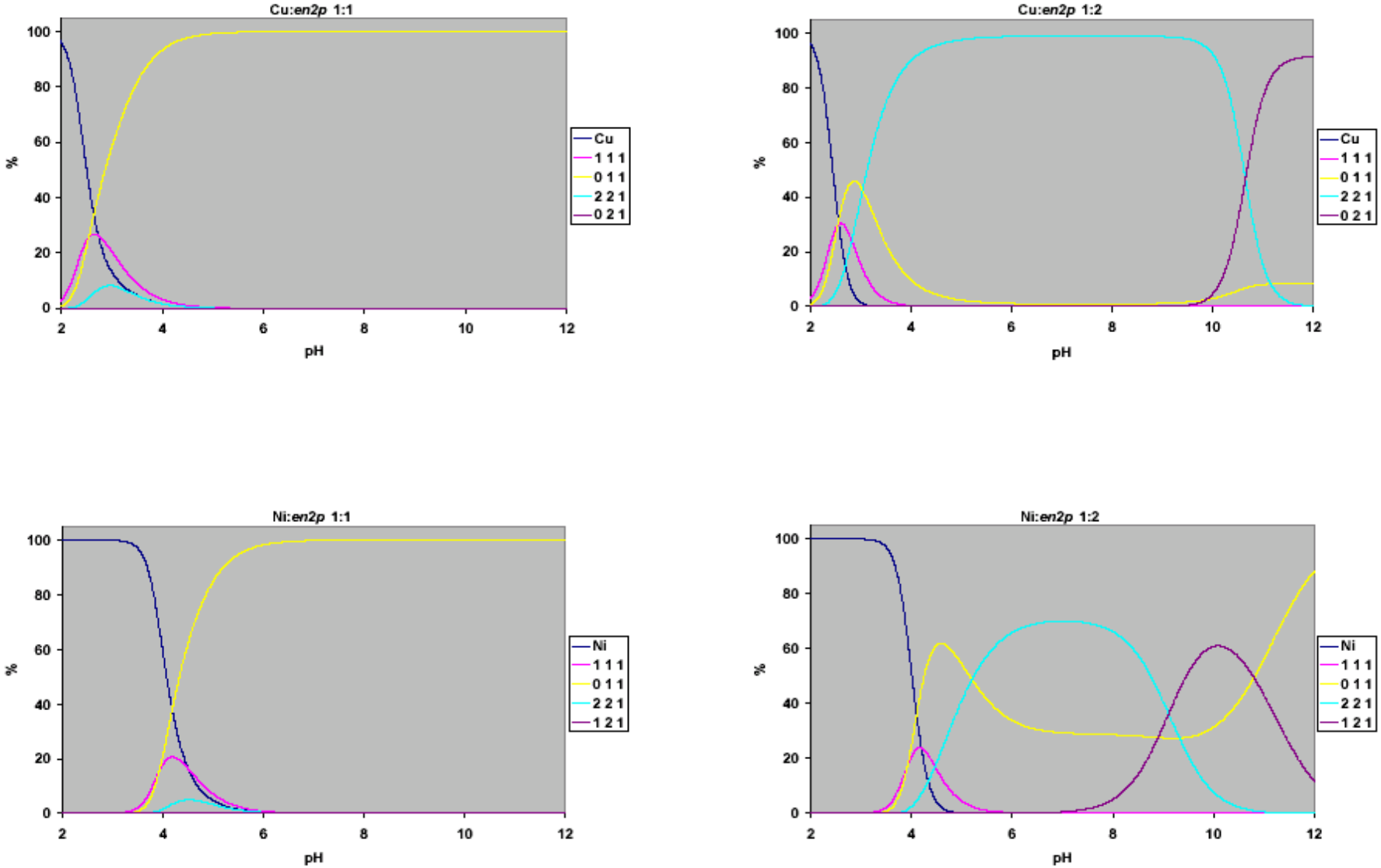
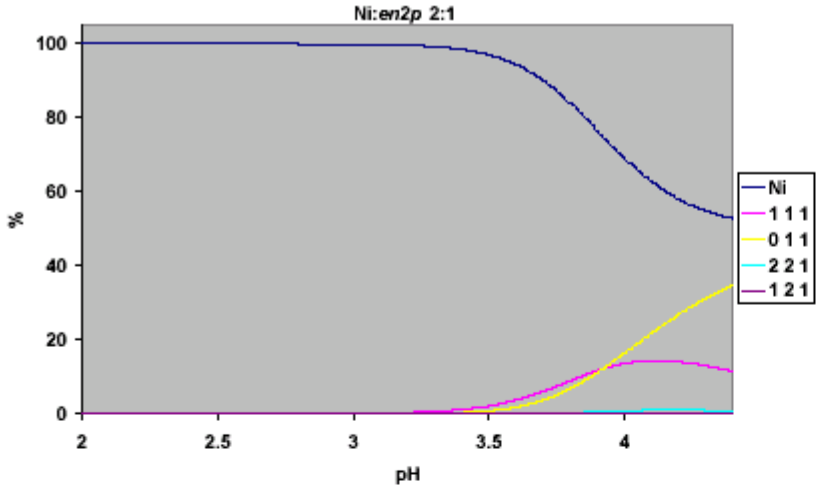
Ref. No.: I200700010

Figure S1: Distribution diagrams of studied metal:Hen$_2$p systems (abundance of the metal on the y axis).

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%
pH
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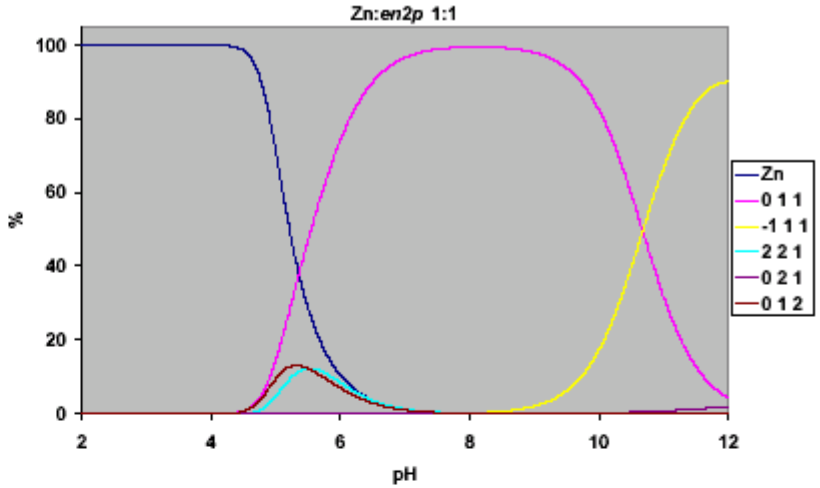
0 1 1
2 2 1
1 2 1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%
pH
Zn
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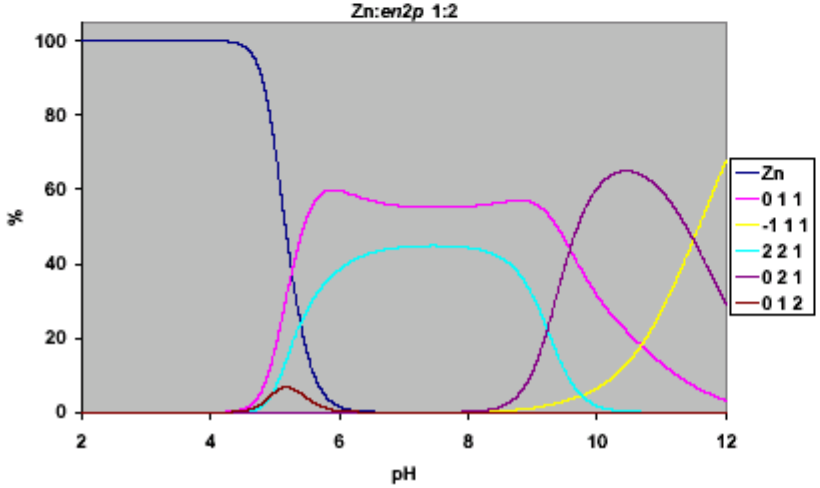
-1 1 1
2 2 1
0 2 1
0 1 2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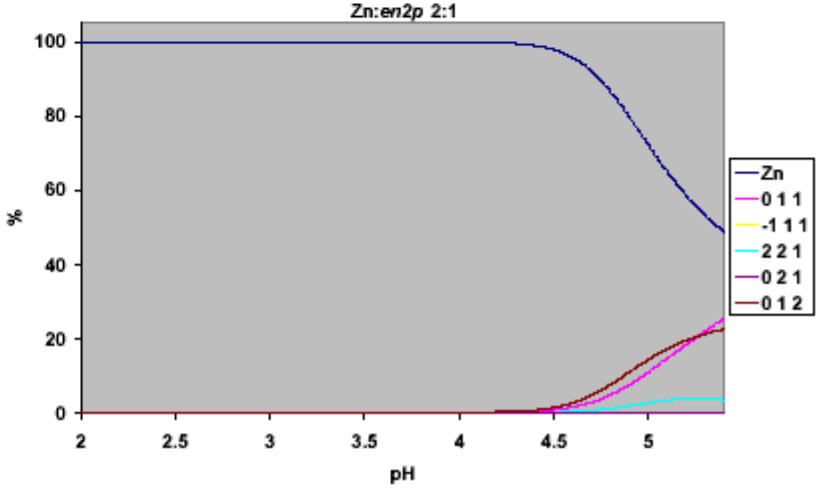
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%
pH
Zn
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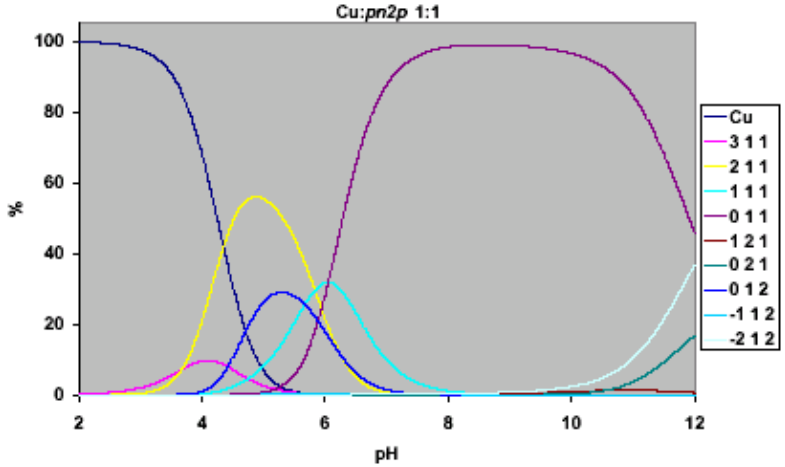
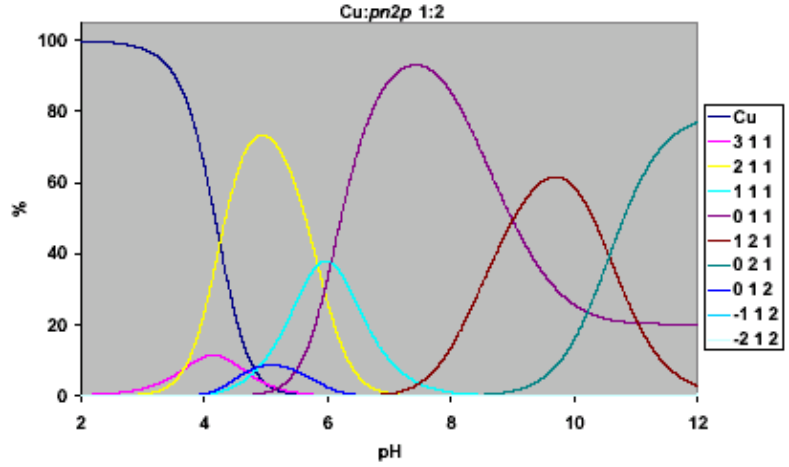
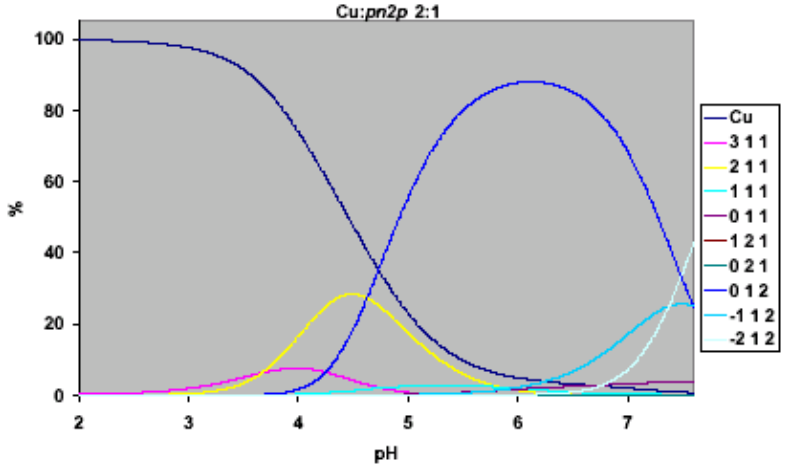
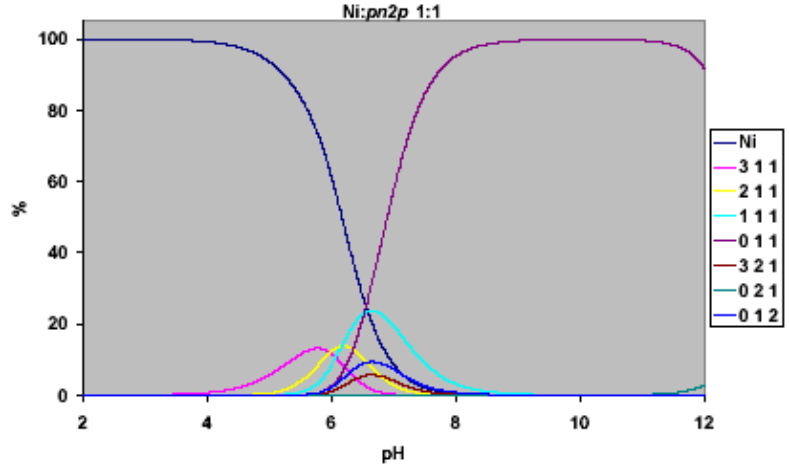
2 2 1
0 2 1
0 1 2

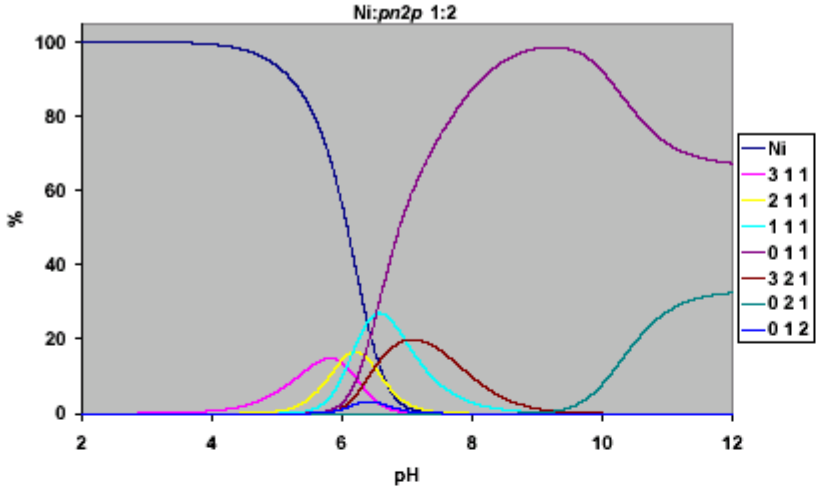
Figure S2: Distribution diagrams of studied metal:Hpn$_2$p systems (abundance of the metal on the y axis).







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%
pH
Ni
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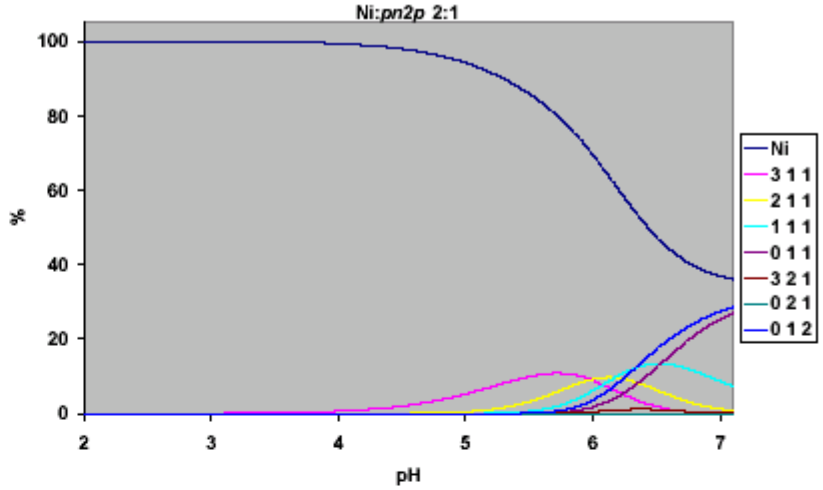
2 1 1
1 1 1
0 1 1
3 2 1
0 2 1
0 1 2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%
pH
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2 1 1
1 1 1
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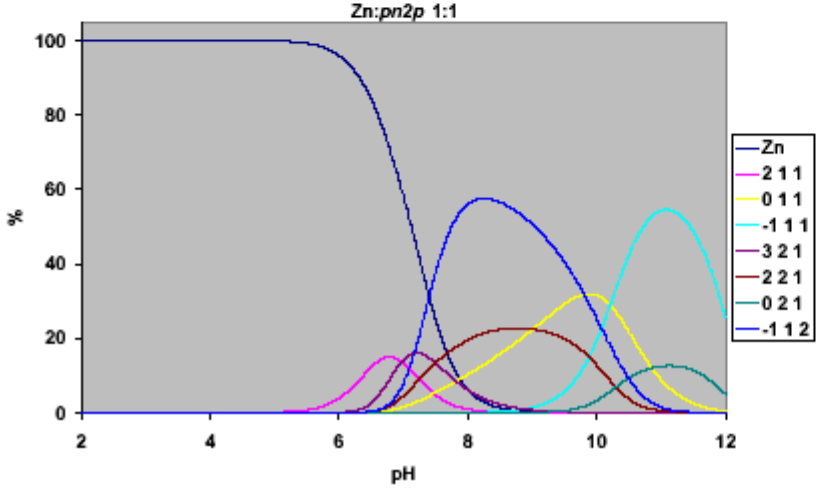
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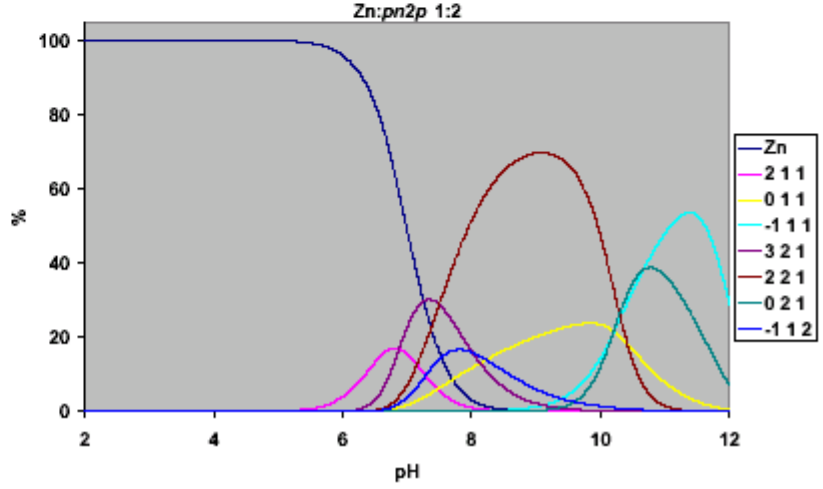
%
pH
Zn
2 1 1
0 1 1
-1 1 1
3 2 1
2 2 1
0 2 1
-1 1 2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%
pH
Zn
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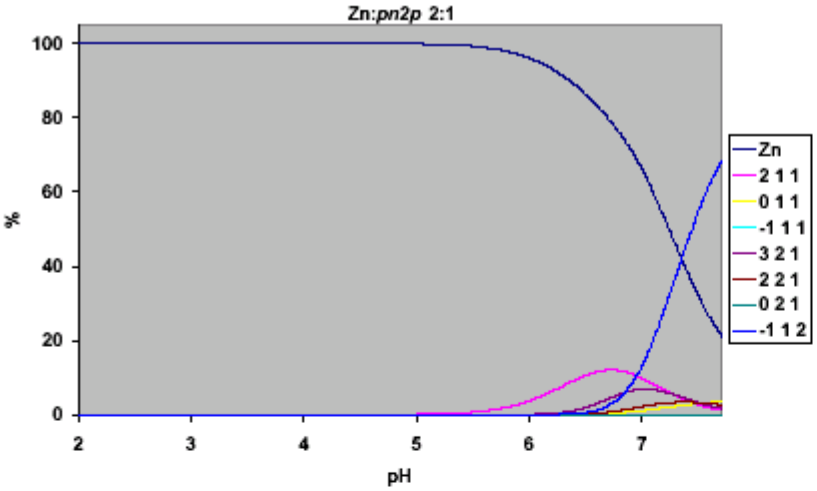
-1 1 1
3 2 1
2 2 1
0 2 1
-1 1 2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100
80
60
40
20
0
%
2
3
4
5
6
7
pH
Zn
2 1 1
0 1 1
-1 1 1
3 2 1
2 2 1
0 2 1
-1 1 2

Table S1: Geometric parameters of coordination polyhedrons in the crystal structures of $(H_4en_2p)[CuCl_4]Cl$ (**5**) and $(H_4en_2p)[ZnCl_4]Cl$ (**6**)

compound 5		**compound 6**	
distances (Å)		**distances (Å)**	
Cu–Cl1	2.213(1)	Zn–Cl1	2.241(1)
Cu–Cl2	2.226(1)	Zn–Cl2	2.2530(9)
Cu–Cl3	2.2643(9)	Zn–Cl3	2.2937(9)
Cu–Cl4	2.345(1)	Zn–Cl4	2.355(1)
angles (°)		**angles (°)**	
Cl1-Cu-Cl2	142.87(7)	Cl1-Zn-Cl2	124.27(5)
Cl1-Cu-Cl3	98.11(4)	Cl1-Zn-Cl3	106.88(4)
Cl1-Cu-Cl4	99.94(5)	Cl1-Zn-Cl4	110.38(4)
Cl2-Cu-Cl3	98.66(4)	Cl2-Zn-Cl3	108.71(3)
Cl2-Cu-Cl4	96.42(4)	Cl2-Zn-Cl4	102.48(4)
Cl3-Cu-Cl4	126.18(4)	Cl3-Zn-Cl4	101.95(3)

Table S2: Geometric parameters of coordination polyhedrons in the crystal structure of $Na_2(NH_4)_4[Cu(en_2p)]_4Br_4(PF_6)_6 \cdot H_2O$ (**7**)

central atom Cu1A		**central atom Cu1B**		**central atom Cu1C**		**central atom Cu1D**	
distances (Å)		**distances (Å)**		**distances (Å)**		**distances (Å)**	
Cu1A–N1A	2.011(4)	Cu1B–N1B	2.010(5)	Cu1C–N1C	2.016(5)	Cu1D–N1D	2.019(4)
Cu1A–N4A	2.062(4)	Cu1B–N4B	2.038(4)	Cu1C–N4C	2.059(4)	Cu1D–N4D	2.043(4)
Cu1A–Br1	2.677(1)	Cu1B–Br2	2.821(1)	Cu1C–Br3	2.684(1)	Cu1D–Br2	2.813(1)
Cu1A–O61B	2.840(5)	Cu1B–O61C	2.733(5)			Cu1D–Br3	3.007(1)
angles (°)		**angles (°)**		**angles (°)**		**angles (°)**	
N1A-Cu1A-N1A$^{\#}$	92.6(3)	N1B-Cu1B-N1B$^{\#}$	91.3(3)	N1C-Cu1C-N1C$^{\#}$	92.0(3)	N1D-Cu1D-N1D$^{\#}$	92.1(3)
N1A-Cu1A-N4A	84.2(2)	N1B-Cu1B-N4B	85.2(2)	N1C-Cu1C-N4C	84.8(2)	N1D-Cu1D-N4D	84.9(2)
N1A-Cu1A-N4A$^{\#}$	172.3(2)	N1B-Cu1B-N4B$^{\#}$	173.4(2)	N1C-Cu1C-N4C$^{\#}$	174.7(2)	N1D-Cu1D-N4D$^{\#}$	174.2(2)
N1A-Cu1A-Br1	92.8(1)	N1B-Cu1B-Br2	93.2(1)	N1C-Cu1C-Br3	95.9(1)	N1D-Cu1D-Br2	91.1(1)
N1A-Cu1A-O61B	87.7(2)	N1B-Cu1B-O61C	97.1(2)			N1D-Cu1D-Br3	93.4(1)
N1A$^{\#}$-Cu1A-N4A	172.3(2)	N1B$^{\#}$-Cu1B-N4B	173.4(2)	N1C$^{\#}$-Cu1C-N4C	174.7(2)	N1D$^{\#}$-Cu1B-N4D	174.2(2)
N1A$^{\#}$-Cu1A-N4A$^{\#}$	84.2(2)	N1B$^{\#}$-Cu1B-N4B$^{\#}$	85.2(2)	N1C$^{\#}$-Cu1C-N4C$^{\#}$	84.8(2)	N1D$^{\#}$-Cu1D-N4D$^{\#}$	84.9(2)
N1A$^{\#}$-Cu1A-Br1	92.8(1)	N1B$^{\#}$-Cu1B-Br2	93.2(1)	N1C$^{\#}$-Cu1C-Br3	95.9(1)	N1D$^{\#}$-Cu1D-Br2	91.1(1)
N1A$^{\#}$-Cu1A-O61B	87.7(2)	N1B$^{\#}$-Cu1B-O61C	97.1(2)			N1D$^{\#}$-Cu1D-Br3	93.4(1)
N4A-Cu1A-N4A$^{\#}$	98.2(2)	N4B-Cu1B-N4B$^{\#}$	97.7(2)	N4C-Cu1C-N4C$^{\#}$	98.0(2)	N4D-Cu1D-N4D$^{\#}$	97.7(2)
N4A-Cu1A-Br1	94.3(1)	N4B-Cu1B-Br2	92.7(1)	N4C-Cu1C-Br3	88.6(1)	N4D-Cu1D-Br2	93.9(1)
N4A-Cu1A-O61B	85.2(1)	N4B-Cu1B-O61C	77.8(1)			N4D-Cu1D-Br3	81.9(1)
N4A$^{\#}$-Cu1A-Br1	94.3(1)	N4B$^{\#}$-Cu1B-Br2	92.7(1)	N4C$^{\#}$-Cu1C-Br3	88.6(1)	N4D$^{\#}$-Cu1D-Br2	93.9(1)
N4A$^{\#}$-Cu1A-O61B	85.2(1)	N4B$^{\#}$-Cu1B-O61C	77.8(1)			N4D$^{\#}$-Cu1D-Br3	81.9(1)
Br1-Cu1A-O61B	179.3(1)	Br2-Cu1B-O61C	165.4(1)			Br2-Cu1D-Br3	173.47(4)

$^{\#}$ means symmetrically related atoms through plane of symmetry of the complex

Table S3: Geometric parameters of coordination polyhedrons in the crystal structure of $Na_{3/2}(NH_4)_2[Zn(en_2p)]_3Br_{5/2}(PF_6)_4 \cdot 3H_2O$ (**8**)

central atom Zn1A		**central atom Zn1B**		**central atom Zn1C**	
distances (Å)		**distances (Å)**		**distances (Å)**	
Zn1A–N1A	2.119(5)	Zn1B–N1B	2.110(6)	Zn1C–N1C	2.107(5)
Zn1A–N4A	2.153(5)	Zn1B–N4B	2.187(5)	Zn1C–N4C	2.166(5)
Zn1A–Br1A	2.373(2)	Zn1B–Br2	2.910(1)	Zn1C–O61B	2.055(6)
		Zn1B–O61A	2.103(6)		
angles (°)		**angles (°)**		**angles (°)**	
N1A-Zn1A-N1A$^{\#}$	99.4(3)	N1B-Zn1B-N1B$^{\#}$	107.3(4)	N1C-Zn1C-N1C$^{\#}$	98.4(3)
N1A-Zn1A-N4A	81.6(2)	N1B-Zn1B-N4B	82.3(2)	N1C-Zn1C-N4C	83.1(2)
N1A-Zn1A-N4A$^{\#}$	163.0(2)	N1B-Zn1B-N4B$^{\#}$	167.6(2)	N1C-Zn1C-N4C$^{\#}$	161.5(2)
N1A-Zn1A-Br1A	99.0(2)	N1B-Zn1B-Br2	80.0(2)	N1C-Zn1C-O61B	96.6(2)
		N1B-Zn1B-O61A	92.3(2)		
N1A$^{\#}$-Zn1A-N4A	163.0(2)	N1B$^{\#}$-Zn1B-N4B	167.6(2)	N1C$^{\#}$-Zn1C-N4C	161.5(2)
N1A$^{\#}$-Zn1A-N4A$^{\#}$	81.6(2)	N1B$^{\#}$-Zn1B-N4B$^{\#}$	82.3(2)	N1C$^{\#}$-Zn1C-N4C$^{\#}$	83.1(2)
N1A$^{\#}$-Zn1A-Br1A	99.0(2)	N1B$^{\#}$-Zn1B-Br2	80.0(3)	N1C$^{\#}$-Zn1C-O61B	96.6(2)
		N1B$^{\#}$-Zn1B-O61A	92.3(2)		
N4A-Zn1A-N4A$^{\#}$	92.5(3)	N4B-Zn1B-N4B$^{\#}$	87.2(3)	N4C-Zn1C-N4C$^{\#}$	89.9(2)
N4A-Zn1A-Br1A	97.6(1)	N4B-Zn1B-Br2	94.3(1)	N4C-Zn1C-O61B	101.6(2)
		N4B-Zn1B-O61A	95.2(2)		
N4A$^{\#}$-Zn1A-Br1A	97.6(1)	N4B$^{\#}$-Zn1B-Br2	94.3(1)	N4C$^{\#}$-Zn1C-O61B	101.6(2)
		N4B$^{\#}$-Zn1B-O61A	95.2(2)		
		Br2-Zn1B-O61A	166.9(2)		

$^{\#}$ means symmetrically related atoms through plane of symmetry of the complex

Table S4: Geometric parameters of coordination polyhedrons in the crystal structure of $Na_2[Cu(pn_2p)]_4Br_2(ClO_4)_4 \cdot 3H_2O$ (**9**)

central atom Cu1A		**central atom Cu1B**		**central atom Cu1C**		**central atom Cu1D**	
distances (Å)		**distances (Å)**		**distances (Å)**		**distances (Å)**	
Cu1A–N1A	2.025(8)	Cu1B–N1B	2.030(8)	Cu1C–N1C	2.15(2)	Cu1D–N1D	2.033(7)
Cu1A–N5A	2.055(7)	Cu1B–N5B	2.068(7)	Cu1C–N5C	2.064(7)	Cu1D–N5D	2.050(7)
Cu1A–O71B	2.333(7)	Cu1B–O71C	2.286(8)	Cu1C–O71D	2.84(1)	Cu1D–O1D	2.142(9)
				Cu1C–Br1C	2.870(3)		
angles (°)		**angles (°)**		**angles (°)**		**angles (°)**	
N1A-Cu1A-N1A$^{\#}$	90.8(5)	N1B-Cu1B-N1B$^{\#}$	84.5(5)	N1C-Cu1C-N1C$^{\#}$	102.2(9)	N1D-Cu1D-N1D$^{\#}$	90.1(4)
N1A-Cu1A-N5A	90.2(3)	N1B-Cu1B-N5B	92.1(3)	N1C-Cu1C-N5C	84.5(5)	N1D-Cu1D-N5D	89.7(3)
N1A-Cu1A-N5A$^{\#}$	174.2(3)	N1B-Cu1B-N5B$^{\#}$	165.7(3)	N1C-Cu1C-N5C$^{\#}$	172.3(5)	N1D-Cu1D-N5D$^{\#}$	163.3(3)
N1A-Cu1A-O71B	90.9(3)	N1B-Cu1B-O71C	99.7(3)	N1C-Cu1C-O71D	90.3(5)	N1D-Cu1D-O1D	97.4(3)
				N1C-Cu1C-Br1C	77.0(5)		
N1A$^{\#}$-Cu1A-N5A	174.2(3)	N1B$^{\#}$-Cu1B-N5B	165.7(3)	N1C$^{\#}$-Cu1C-N5C	172.3(5)	N1D$^{\#}$-Cu1B-N5D	163.3(3)
N1A$^{\#}$-Cu1A-N5A$^{\#}$	90.2(3)	N1B$^{\#}$-Cu1B-N5B$^{\#}$	92.1(3)	N1C$^{\#}$-Cu1C-N5C$^{\#}$	84.5(5)	N1D$^{\#}$-Cu1D-N5D$^{\#}$	89.7(3)
N1A$^{\#}$-Cu1A-O71B	90.9(3)	N1B$^{\#}$-Cu1B-O71C	99.7(3)	N1C$^{\#}$-Cu1C-O71D	90.3(5)	N1D$^{\#}$-Cu1D-O1D	97.4(3)
				N1C$^{\#}$-Cu1C-Br1C	77.0(5)		
N5A-Cu1A-N5A$^{\#}$	88.3(4)	N5B-Cu1B-N5B$^{\#}$	87.8(4)	N5C-Cu1C-N5C$^{\#}$	88.6(4)	N5D-Cu1D-N5D$^{\#}$	85.8(4)
N5A-Cu1A-O71B	94.9(2)	N5B-Cu1B-O71C	94.5(2)	N5C-Cu1C-O71D	93.5(3)	N5D-Cu1D-O1D	99.2(3)
				N5C-Cu1C-Br1C	101.2(2)		
N5A$^{\#}$-Cu1A-O71B	94.9(2)	N5B$^{\#}$-Cu1B-O71C	94.5(2)	N5C$^{\#}$-Cu1C-O71D	93.5(3)	N5D$^{\#}$-Cu1D-O1D	99.2(3)
				N5C$^{\#}$-Cu1C-Br1C	101.2(2)		
				O71D-Cu1C-Br1C	159.4(2)		

$^{\#}$ means symmetrically related atoms through plane of symmetry of the complex

Table S5: Geometric parameters of coordination polyhedrons in the crystal structure of $[Ni_4(pn_2p)_4](ClO_4)_4 \cdot 7H_2O$ (**10**)

central atom Ni1		**central atom Ni2**		**central atom Ni3**		**central atom Ni4**	
distances (Å)		**distances (Å)**		**distances (Å)**		**distances (Å)**	
Ni1–N1A	2.107(3)	Ni2–N1B	2.092(3)	Ni3–N1C	2.110(3)	Ni4–N1D	2.114(3)
Ni1–N5A	2.138(3)	Ni2–N5B	2.134(3)	Ni3–N5C	2.137(4)	Ni4–N5D	2.133(3)
Ni1–N9D	2.108(3)	Ni2–N9A	2.132(3)	Ni3–N9B	2.125(3)	Ni4–N9C	2.102(3)
Ni1–N13D	2.100(3)	Ni2–N13A	2.097(3)	Ni3–N13B	2.080(4)	Ni4–N13C	2.082(3)
Ni1–O71A	2.064(2)	Ni2–O71B	2.069(2)	Ni3–O71C	2.105(2)	Ni4–O71D	2.102(2)
Ni1–O72D	2.204(2)	Ni2–O72A	2.149(2)	Ni3–O72B	2.132(3)	Ni4–O72C	2.140(2)
angles (°)		**angles (°)**		**angles (°)**		**angles (°)**	
N1A-Ni1-N5A	91.5(1)	N1B-Ni2-N5B	92.6(1)	N1C-Ni3-N5C	92.2(1)	N1D-Ni4-N5D	92.9(1)
N1A-Ni1-N9D	96.6(1)	N1B-Ni2-N9A	99.1(1)	N1C-Ni3-N9B	97.4(1)	N1D-Ni4-N9C	97.2(1)
N1A-Ni1-N13D	90.7(1)	N1B-Ni2-N13A	89.5(2)	N1C-Ni3-N13B	91.1(2)	N1D-Ni4-N13C	90.2(1)
N1A-Ni1-O71A	174.6(1)	N1B-Ni2-O71B	174.5(1)	N1C-Ni3-O71C	174.1(1)	N1D-Ni4-O71D	175.8(1)
N1A-Ni1-O72D	82.6(1)	N1B-Ni2-O72A	83.6(1)	N1C-Ni3-O72B	84.0(1)	N1D-Ni4-O72C	83.0(1)
N5A-Ni1-N9D	166.9(1)	N5B-Ni2-N9A	165.6(1)	N5C-Ni3-N9B	166.6(1)	N5D-Ni4-N9C	164.9(1)
N5A-Ni1-N13D	95.1(1)	N5B-Ni2-N13A	95.2(1)	N5C-Ni3-N13B	94.5(2)	N5D-Ni4-N13C	96.1(1)
N5A-Ni1-O71A	85.52(9)	N5B-Ni2-O71B	84.8(1)	N5C-Ni3-O71C	85.1(1)	N5D-Ni4-O71D	84.9(1)
N5A-Ni1-O72D	87.78(9)	N5B-Ni2-O72A	89.4(1)	N5C-Ni3-O72B	87.1(1)	N5D-Ni4-O72C	85.4(1)
N9D-Ni1-N13D	95.1(1)	N9A-Ni2-N13A	93.4(1)	N9B-Ni3-N13B	94.7(2)	N9C-Ni4-N13C	95.1(1)
N9D-Ni1-O71A	85.6(1)	N9A-Ni2-O71B	82.9(1)	N9B-Ni3-O71C	84.4(1)	N9C-Ni4-O71D	84.3(1)
N9D-Ni1-O72D	83.04(9)	N9A-Ni2-O72A	83.59(9)	N9B-Ni3-O72B	84.6(1)	N9C-Ni4-O72C	84.8(1)
N13D-Ni1-O71A	94.1(1)	N13A-Ni2-O71B	95.6(1)	N13B-Ni3-O71C	94.4(1)	N13C-Ni4-O71D	93.6(1)
N13D-Ni1-O72D	172.7(1)	N13A-Ni2-O72A	171.8(1)	N13B-Ni3-O72B	174.8(1)	N13C-Ni4-O72C	173.1(1)
O71A-Ni1-O72D	92.80(9)	O71B-Ni2-O72A	91.53(9)	O71C-Ni3-O72B	90.6(1)	O71D-Ni4-O72C	93.32(9)

Figure S3: $(H_4en_2p)^{3+}$ cation in the structure of $Hen_2p{\cdot}3HCl$ (**4**).

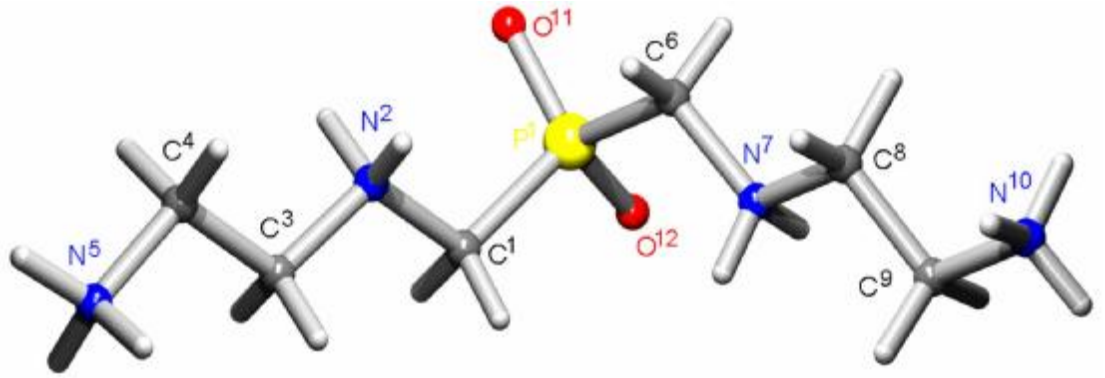


Figure S4: The independent unit of $(H_4en_2p)[CuCl_4]Cl$ (**5**).

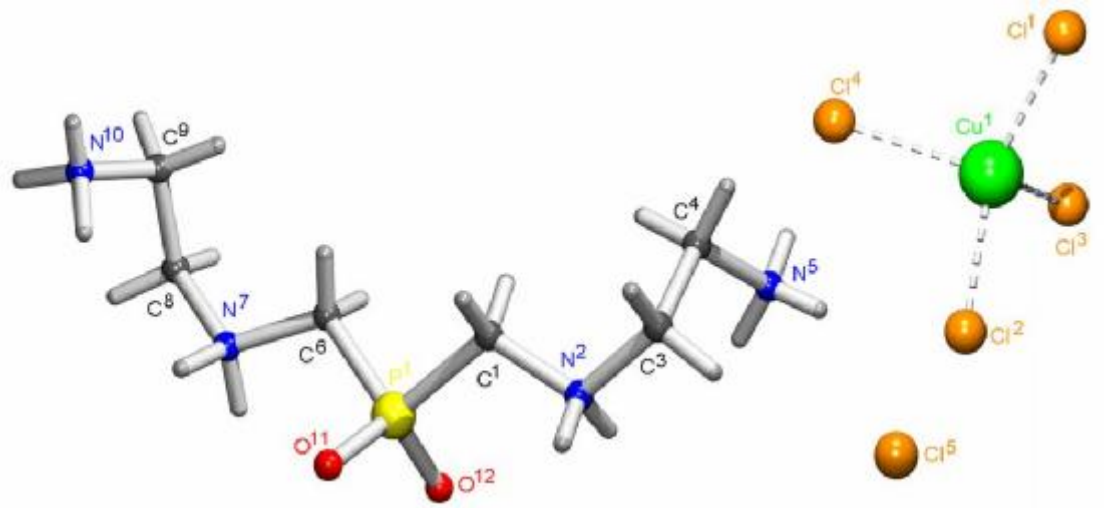


Figure S5: Complex framework found in the crystal structure of $Na_2(NH_4)_4[Cu(en_2p)]_4Br_4(PF_6)_6 \cdot H_2O$ (**7**).

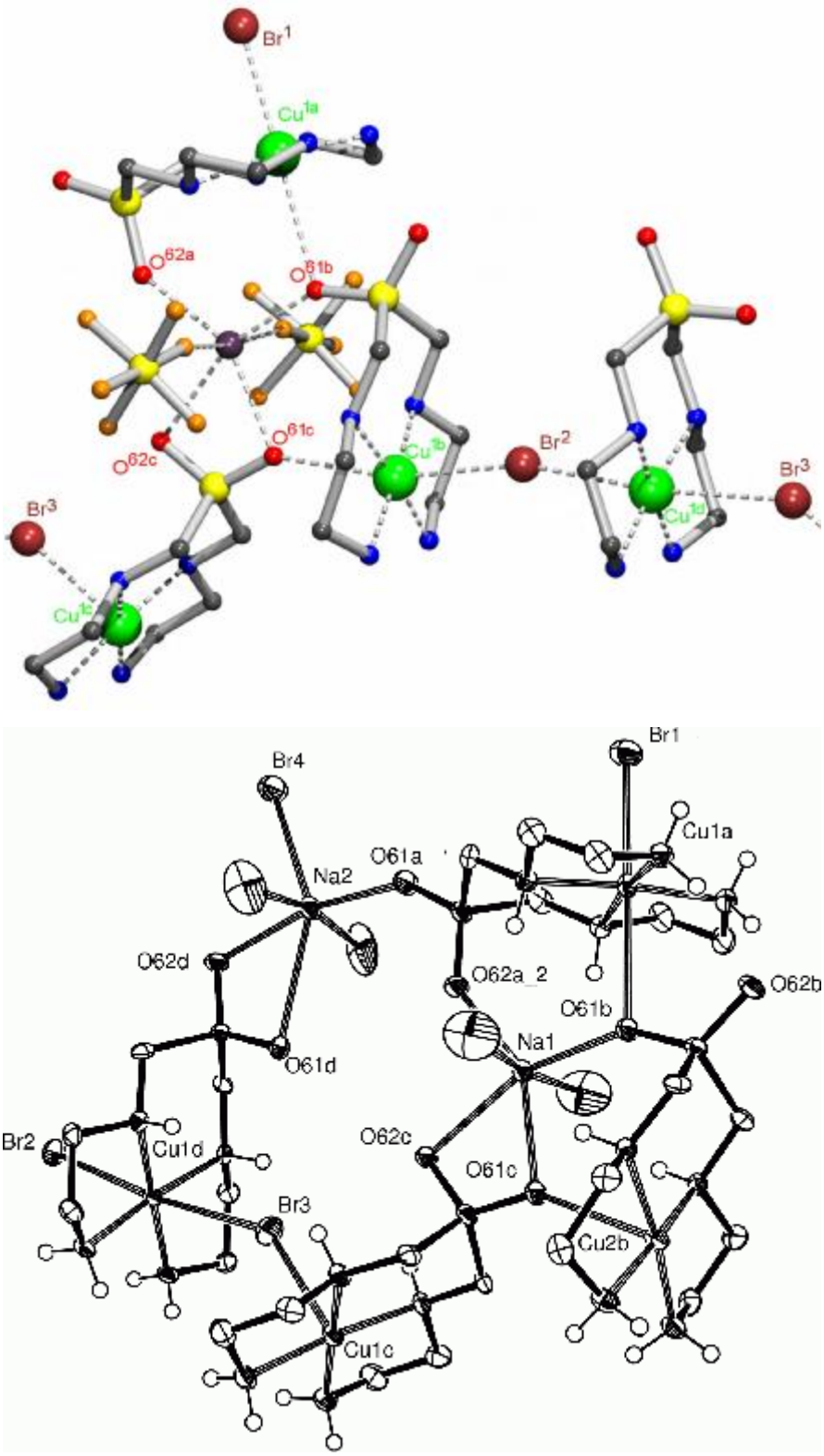
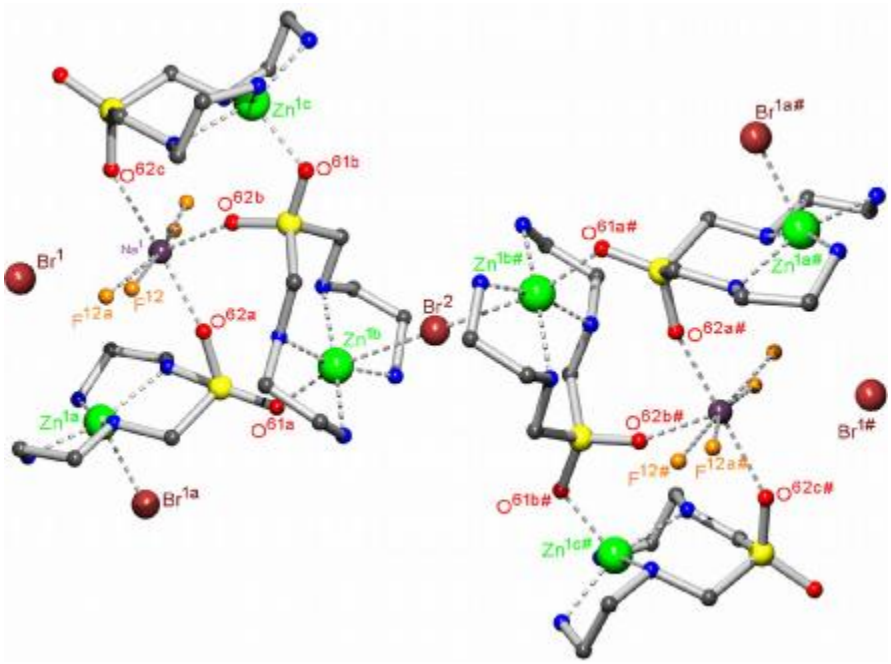


Figure S6: Complex framework found in the crystal structure of $Na_{3/2}(NH_4)_2[Zn(en_2p)]_3Br_{5/2}(PF_6)_4 \cdot 3H_2O$ (**8**). Two structural units are displayed. Fluorine atoms coordinated to the Na^+ ion belong to the hexafluorophosphate anions.



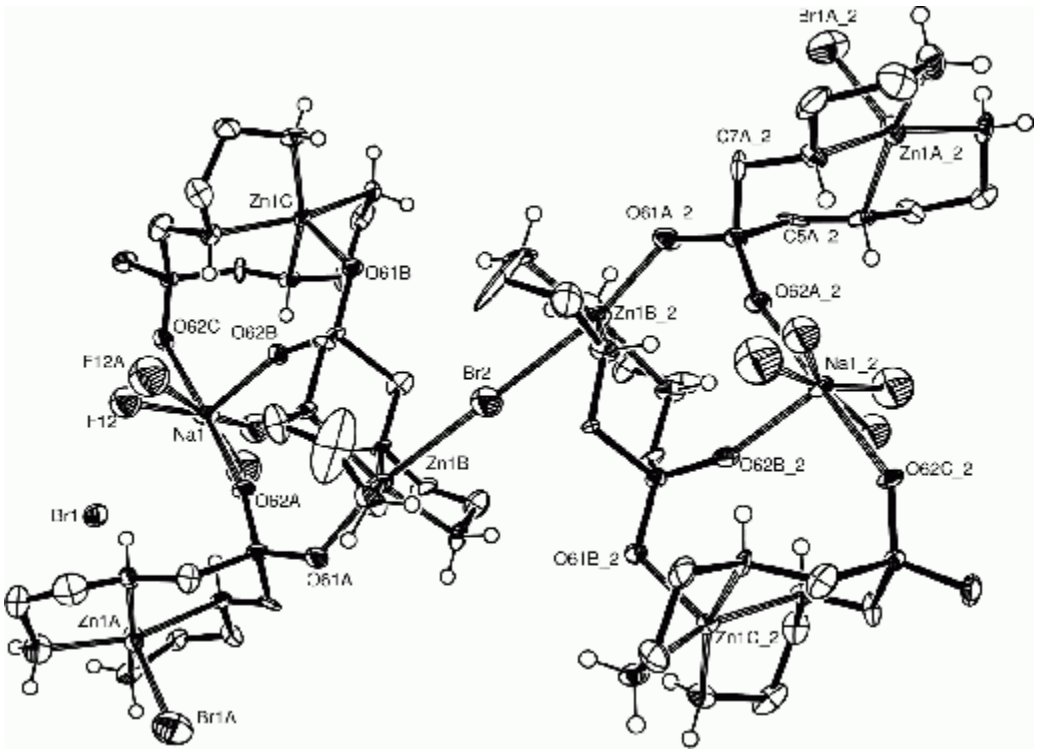
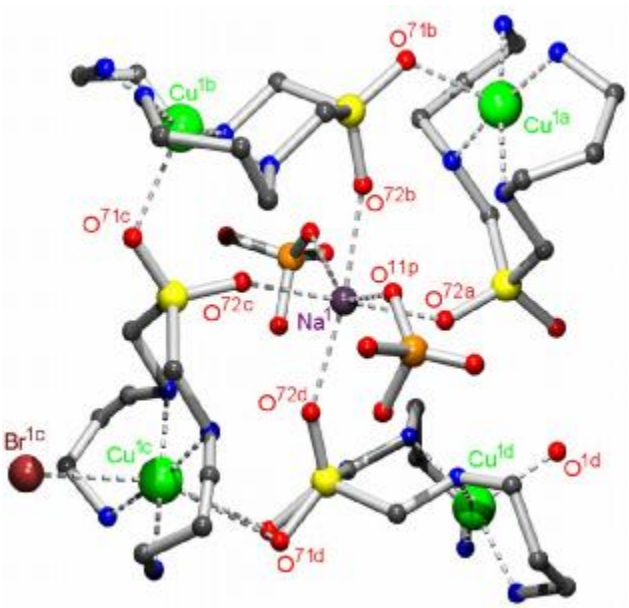


Figure S7: Complex framework found in the crystal structure of $Na_2[Cu(pn_2p)]_4Br_2(ClO_4)_4 \cdot 3H_2O$ (**9**).



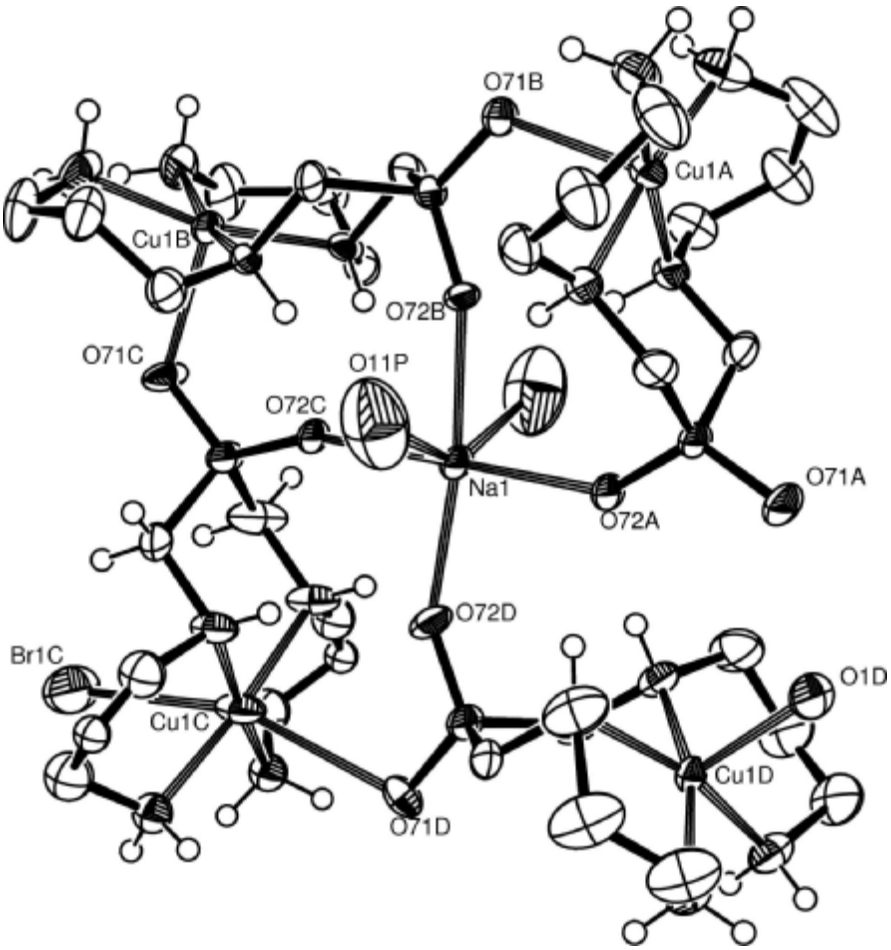


Figure S8: Structure of the $[Ni_4(pn_2p)_4]^{4+}$ complex cation.