Electronic Supplementary Information

Structurally Characterised New Twisted Conformer for Cyclen, Controlled by Metal ion Complexation as Seen in Ni^{II} and Cu^{II} Complexes with halides and pseudohalides.

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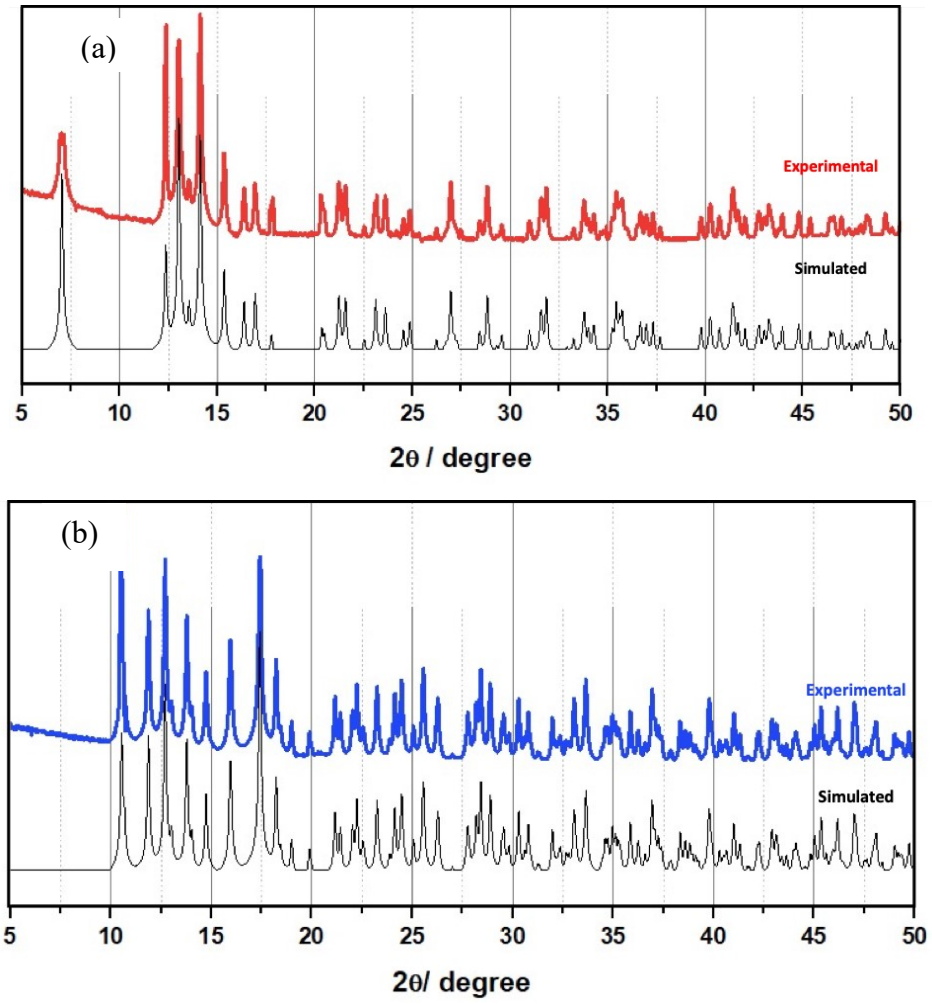

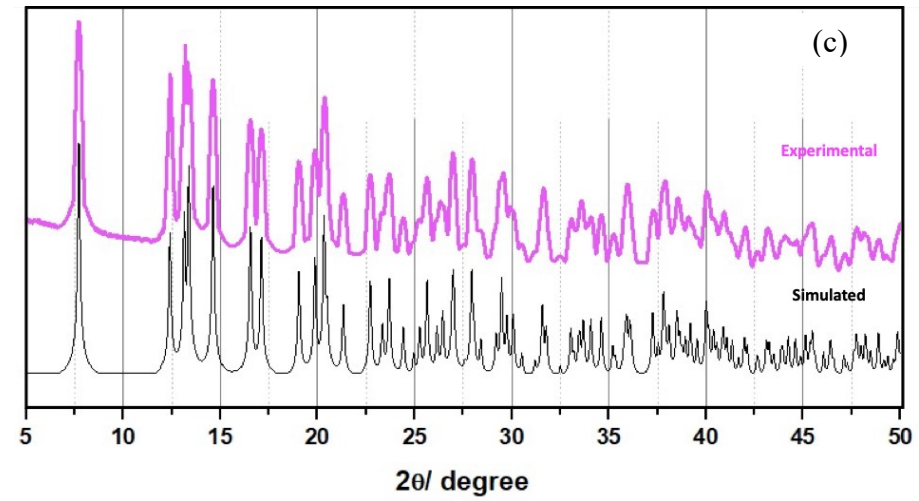
(c)
Experimental
Simulated
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25
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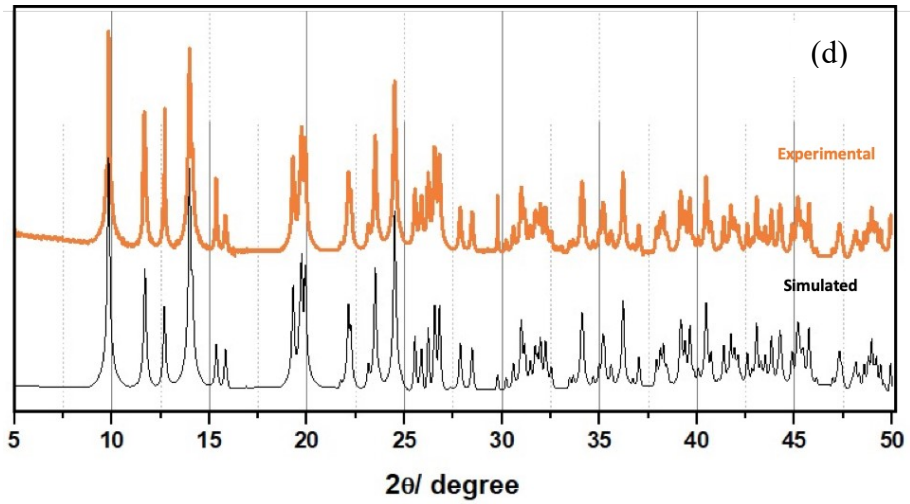
2θ/ degree


(d)
Experimental
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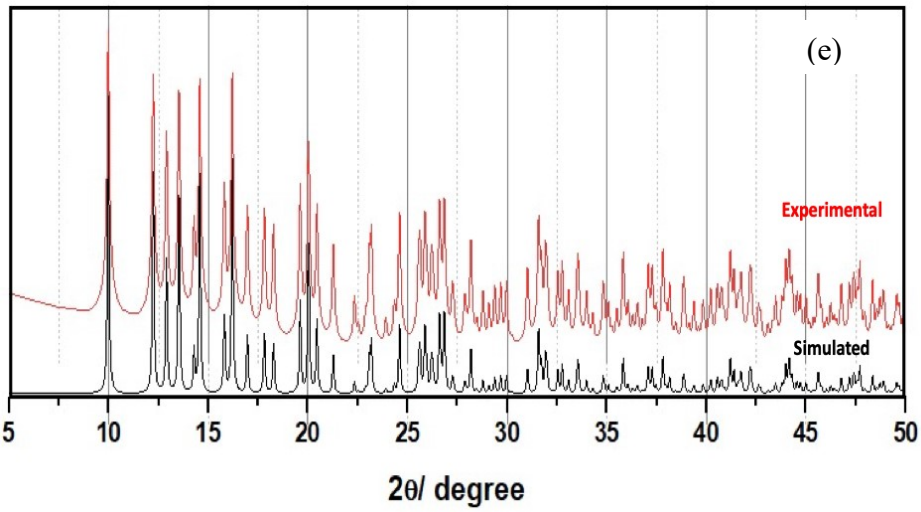
(e)
Experimental
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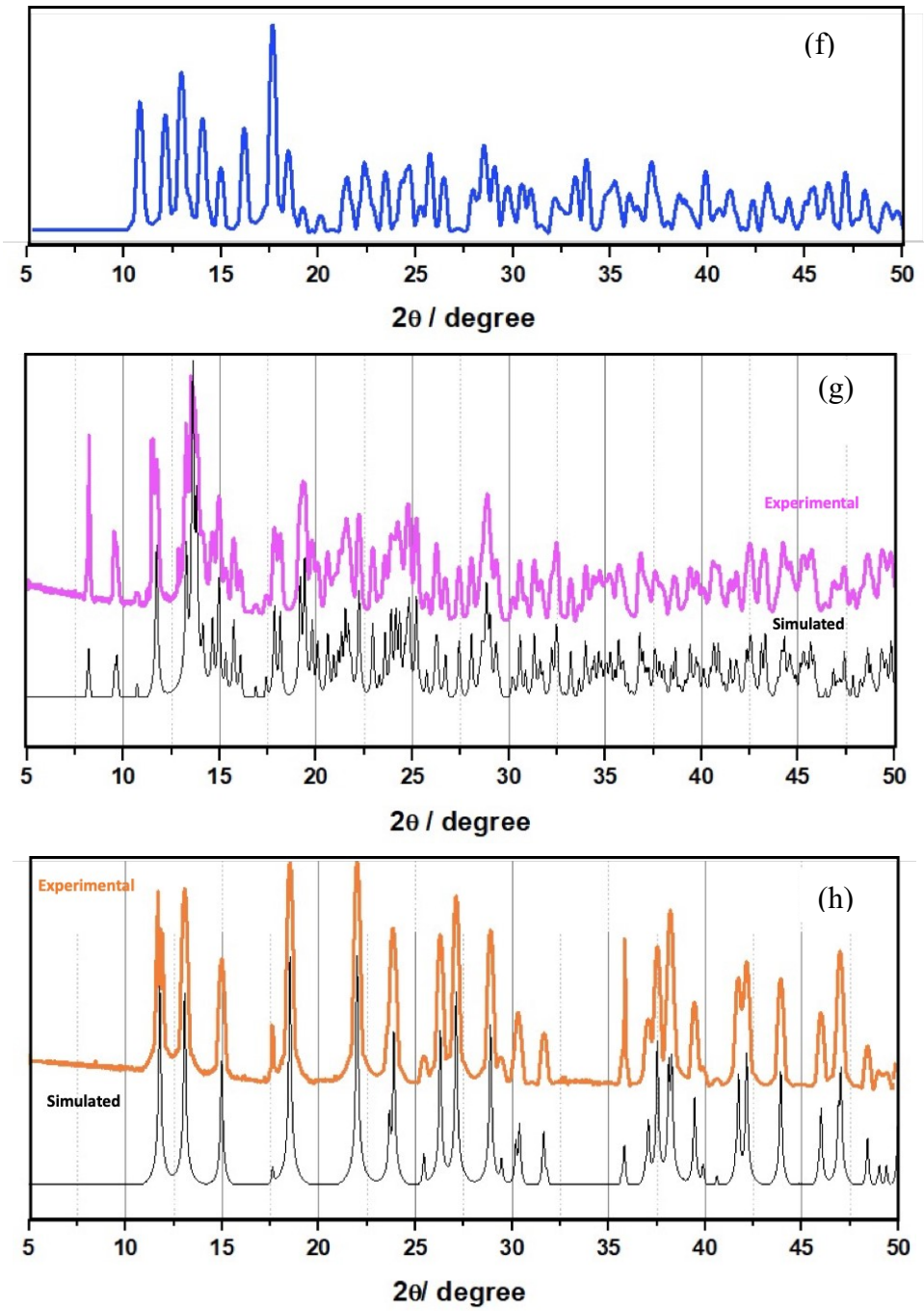


Figure S1. PXRD patterns for the title complexes (a) [**Ni1**]; (b) [**Ni2**]; (c) [**Ni3**]; (d) [**Ni4**]; (e) [**Cu1**]; (f) [**Cu2**]; (g) [**Cu3**]; (h) [**Cu4**]. The experimental patterns of each complex is matched with its corresponding simulated PXRD pattern from the crystal data. The experimental PXRD pattern of complex [**Cu2**] is only presented as its simulated pattern is not available due to lack of SCXRD data.

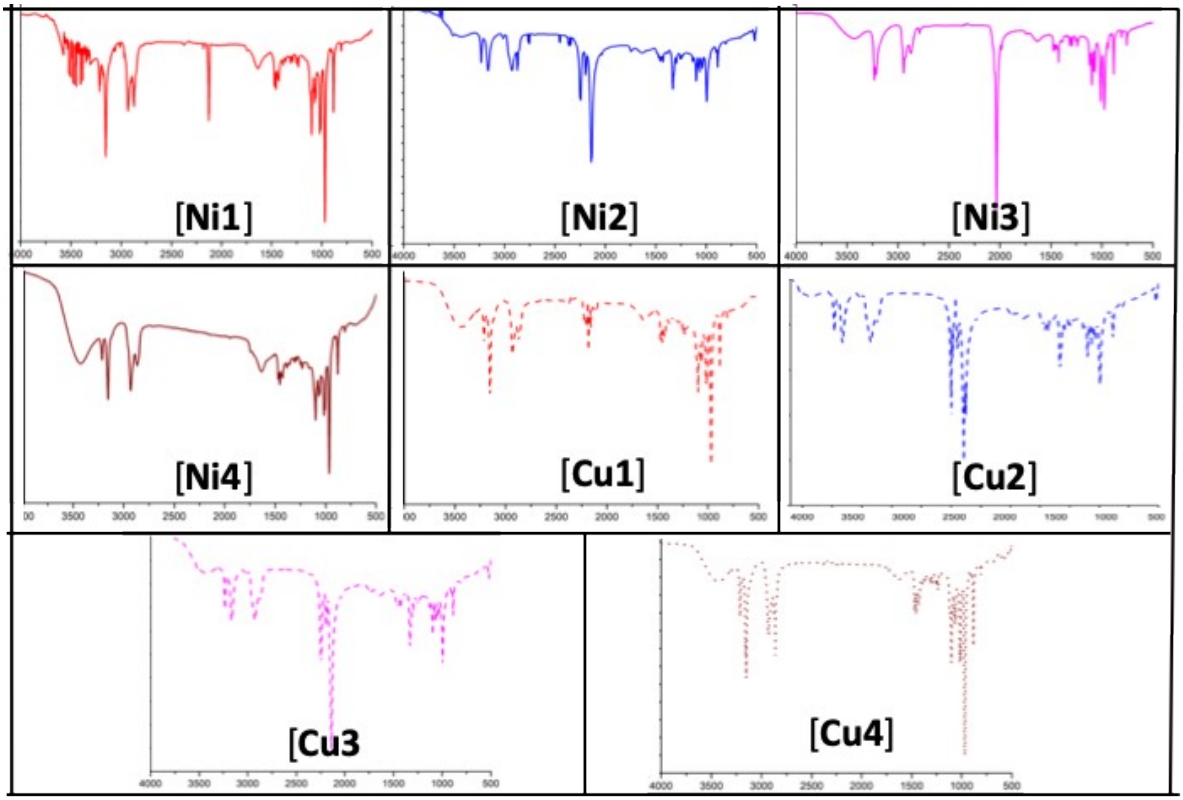


Figure S2. FTIR spectra for the title complexes.

Table S1. Selected bond lengths (Å), angles (°) and important hydrogen bonding interactions (Å) for title complexes.

[Ni1]

Bond lengths (Å)

Ni1-N1	2.085(11)	Ni1-N2	2.117(10)	Ni1-N3	2.072(12)	Ni1-N2^{I}	2.117(10)
Ni1-N4	2.100(6)	Ni1-N6^{II}	2.108(5)	Ni1 -N2^{II}	2.135(10)	Ni1-N3^{II}	2.087(11)
Ni1-N2^{III}	2.135(11)	Ni1-N6	2.108(5)	Ni1-N4^{II}	2.100(6)	Ni1-N1^{II}	2.079(11)
Ni1-Ni2	5.313(11)						

Bond angles (°)

N1-Ni1-N2	85.0(5)	N2-Ni-N3	79.3(4)	N3-Ni-N2^{I}	79.3(4)
N2^{I}-Ni-N1	85.0(5)	N2-Ni-N4	104.2(5)	N4-Ni-N6^{II}	87.6(2)
N6^{II}-Ni-N2^{I}	96.7(6)	N2^{I}-Ni-N2	153.6(10)	N1^{II}-Ni1-N2^{II}	85.0(5)
N2^{II}-Ni1-N3^{II}	79.3(4)	N3^{II}-Ni1-N2^{III}	79.3(4)	N2^{III}-Ni1^{II}-N1^{II}	85.0(5)
N2^{II}-Ni1^{II}-N4^{II}	105.1(7)	N4^{II}-Ni1^{II}-N6	87.6(2)	N6-Ni1^{II}-N2^{III}	96.7(6)
N2^{III}-Ni1^{II}-N2^{II}	153.6(10)				

[Ni2]

Bond lengths (Å)

Ni-N1	2.084(3)	Ni-N2	2.127(3)	Ni-N3	2.081(3)	Ni-N4	2.130(3)
Ni-N5	2.109(3)	Ni-N8	2.066(3)				

Bond angles (°)

N1-Ni-N2	81.18(12)	N2-Ni-N3	83.63(13)	N3-Ni-N4	83.32(13)
N4-Ni-N1	81.15(12)	N1-Ni-N5	89.50(13)	N5-Ni-N8	84.88(13)
N8-Ni-N3	88.09(13)	N3-Ni-N1	97.65(13)		

Hydrogen Bonding Interactions

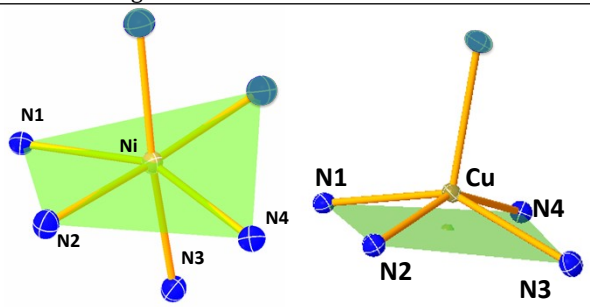
D-H····A	D-H	H····A	D····A	<(DHA)
N1-H1····N10^{I}	1.00	2.10	3.023(5)	152.4
N4-H4····N10^{II}	1.00	2.23	3.167(5)	156.3
N3-H3····N7^{III}	1.00	2.07	3.046(5)	164.2
C8-H8B····N7^{IV}	0.99	2.67	3.590(5)	154.0

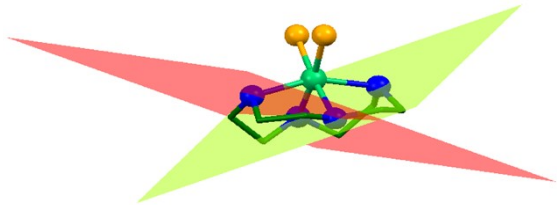
[Ni3]									
Bond lengths (Å)									
Ni-N1	2.089(7)	Ni-N2	2.130(7)	Ni-N3	2.102(7)	Ni-N4	2.158(7)		
Ni-N5	2.085(8)	Ni-N6	2.071(7)						
Bond angles (°)									
N1-Ni-N2	82.6(3)	N2-Ni-N3	81.73(9)	N3-Ni-N4	81.61(5)				
N4-Ni-N1	82.03(9)	N1-Ni-N5	84.13(10)	N5-Ni-N8	87.630(3)				
N8-Ni-N3	87.23(10)	N3-Ni-N1	101.14(6)						
Hydrogen Bonding Interactions									
D-H····A	D-H	H····A	D····A	<(DHA)					
N2-H1····S2^{I}	1.00	2.62	3.481(4)	144.3					
N4-H4····S2^{II}	1.00	2.870	3.553(4)	156.10					
N1-H1····S2^{III}	1.00	2.753	3.620(4)	145.16					
N3-H3····S1^{IV}	1.00	2.76	3.578(6)	158.60					
[Ni4]									
Bond lengths (Å)									
Ni-N1	2.060(4)	Ni-N2	2.105(3)	Ni-N3	2.036(4)	Ni-N2^{I}	2.105(3)	Ni-O1	2.157(4)
Ni-O2	2.076(4)								
Bond angles (°)									
N1-Ni-N2	82.74(9)	N2-Ni-N3	85.03(9)	N3-Ni-N2^{I}	85.03(9)	N2^{I}-Ni-N1	82.74(9)		
N1-Ni-N3	102.40(17)	N1-Ni-O1	99.17(9)	O1-Ni-O2	62.52(13)	O2-Ni-N3	99.17(9)		
Hydrogen Bonding Interactions									
D-H····A	D-H	H····A	D····A	<(DHA)					
N1-H1····Br1	1.00	2.40	3.346(4)	157.2					
[Cu1]									
Bond lengths (Å)									
Cu-N1	2.0119(12)	Cu-N2	2.0217(12)	Cu-N3	2.0328(12)	Cu-N4	2.0395(12)	Cu-N5	2.1032(12)
Bond angles (°)									
N1-Cu-N2	86.18(5)	N2-Cu-N3	85.77(5)	N3-Cu-N4	85.85(5)	N4-Cu-N1	86.42(5)		
Hydrogen Bonding Interactions									
D-H····A	D-H	H····A	D····A	<(DHA)					
N1-H1····N10^{I}	0.98	2.03	2.9734(18)	162.0					
N3-H3····N8	0.98	2.12	3.0523(18)	157.2					
N4-H4····N10^{II}	0.98	2.06	2.9718(17)	153.5					
[Cu3]									
Bond lengths (Å)									
Cu1A-N1A	2.021(5)	Cu1A-N2A	2.031(5)	Cu1A -N3A	2.025(5)	Cu1A -N4A	2.014(5)		
Cu1A-S1A	2.4555(19)	Cu1B-N1B	2.033(5)	Cu1B -N2B	2.038(5)	Cu1B -N3B	2.027(5)		
Cu1B -N4B	2.041(5)	Cu1B -N5B	2.077(6)						
Bond angles (°)									
N1A-Cu1A-N2A	85.6(2)	N2A-Cu1A-N3A	86.1(2)	N3A-Cu1A-N4A	85.7(2)				
N4A-Cu1A-N1A	85.5(2)	N1B-Cu1B-N2B	85.4(2)	N2B-Cu1B-N3B	84.8(2)				
N3B-Cu1B-N4B	85.2(2)	N4B-Cu1B-N1B.	85.5(2)						
Hydrogen Bonding Interactions									
D-H····A	D-H	H····A	D····A	<(DHA)					
N4A-H4A····S1C^{I}	0..98	2.37	3.318(5)	163.3					
N1B-H1B····N1C^{I}	0.98	2.05	2.957(8)	153.2					
N3A-H3A····S1D^{II}	0.98	2.49	3.439(6)	162.2					
N3B-H3B····S1D^{III}	0.98	2.40	3.338(5)	159.6					
[Cu4]									
Bond lengths (Å)									
Cu-N1	2.031(2)	Cu-Br1	2.5313(5)						
Bond angles (°)									
N1-Cu-N1^{I}	85.10(3)								
Hydrogen Bonding Interactions									
D-H····A	D-H	H····A	D····A	<(DHA)					
N1-H1····Br2^{I}	0.89	2.53	3.319(2)	148.5					

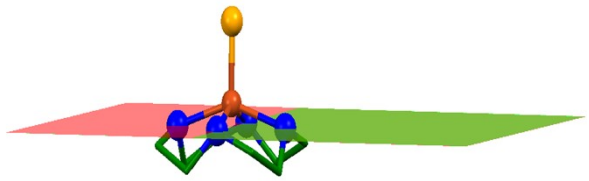
Symmetry codes used to generate equivalent atoms: [I] = x, -y, z; [II] = -x+1, y, -z+1; [III] = -x+1, -y, -z+1 for [**Ni1**]; [I]1/2-X, 1-Y, 1/2+Z; [II]X, 3/2-Y, 1/2+Z; [III]-1/2+X, 3/2-Y, 1-Z ; [IV]1-X, -1/2+Y, 3/2-Z for [**Ni2**]; [I]1/3+Y-X, 2/3-X, -1/3+Z; [II]1-Y, 1-X, -1/2+Z; [III]-1/3+X, 1/3+X-Y, -1/6+Z; [IV]2/3-Y, 1/3+X+Y, 1/3+Z for [**Ni3**]; [I] = x, -y, z for [**Ni4**]; [I]=-x+1, -y+1, -z+1; [II] = x-1, y, z for [**Cu1**]; [I]-1/2+x, ½-y, 1-z; [II]2-x, 1/2+y, ½-z; [III]2-x, -1/2+y, ½-z for [**Cu3**]; [I] = x, 3/2-y, z for [**Cu4**].

Table S2. Dihedral angle between four nitrogen atoms of cyclen and deviation of metal from the basal plane in the title complexes. The ligands nitrogen's are shown in ink blue and anionic nitrogen in teal blue color.`

Complex	Dihedral angle between four nitrogen atoms of the ligand (º)	Deviation of metal ion from the basal plane (Å)
[Ni1]	51.5; 53.7	0.182(1)
[Ni2]	52.1	0.167(11)
[Ni3]	54.6	0.121(2)
[Ni4]	51.7	0.144(3)
[Cu1]	2.7	0.533(2)
[Cu3]	0.2; 0.0	0.553(2); 0.587(1)
[Cu4]	0.0	0.592(2)

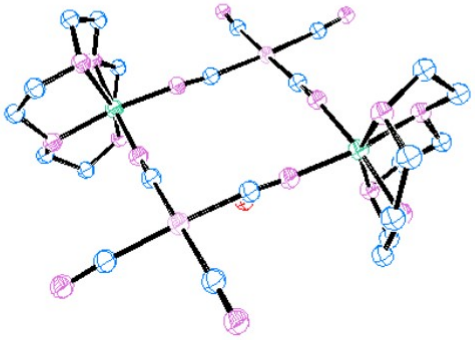
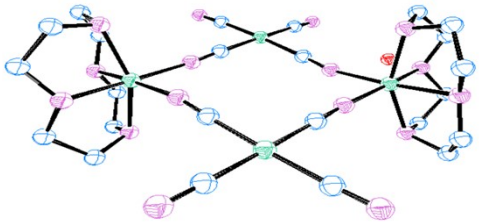
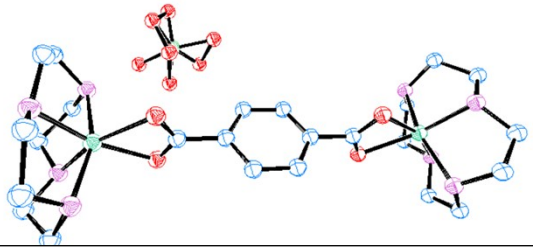






Ni Complexes | Cu Complexes

Table S3. Selected distances and angles for reported complexes of Ni(II) with cyclen.

S.No.	Complex	Ni-N_{cy} (Å)	Ni-Ni (Å)	Dihedral angle (º)
1.	 $[Ni(cyclen)]_2[Pt(CN)_4]_2{\cdot}6H_2O$[S1]	2.07-2.14	7.462	39.300 38.291
2.	 $[Ni(cyclen)]_2[Ni(CN)_4]_2{\cdot}6H_2O$[S1]	2.07-2.13	7.245	38.484 38.231
		2.02-2.11	8.610	36.217 35.829

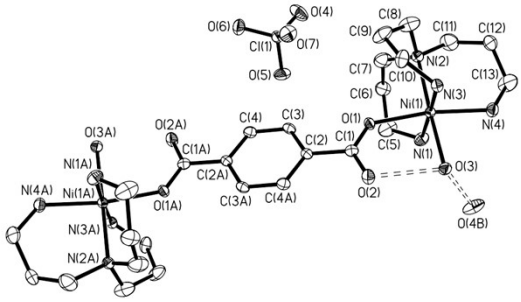
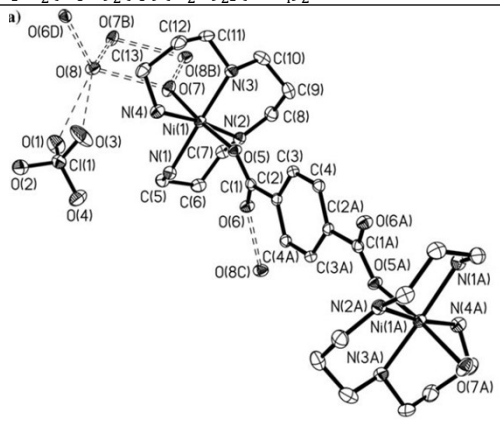
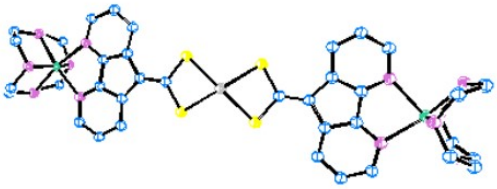
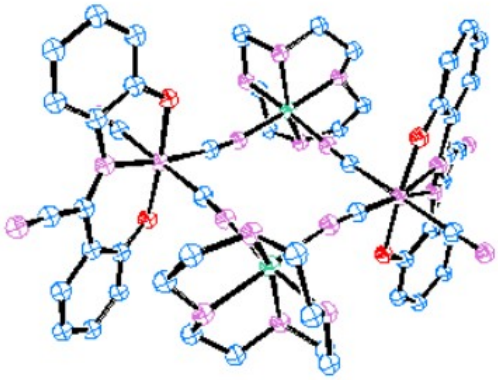
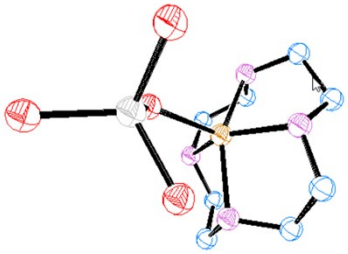
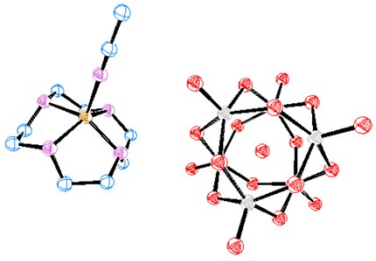
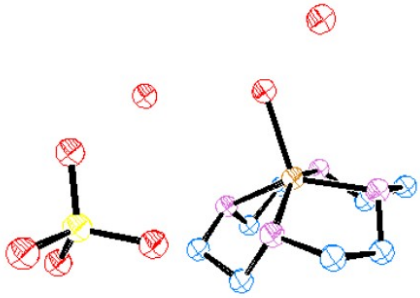
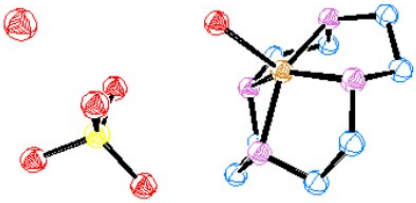
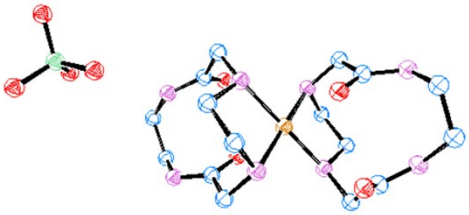
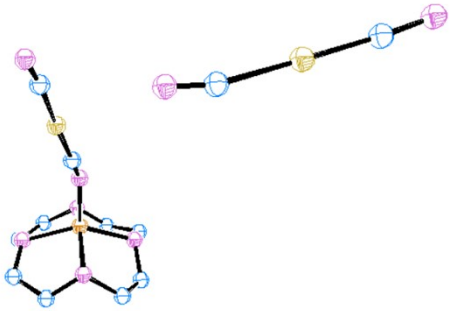
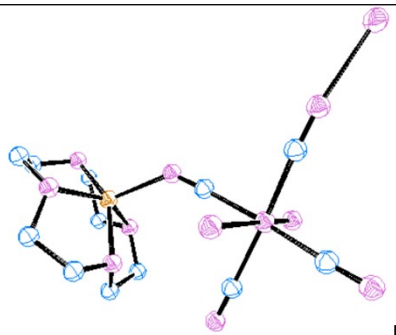
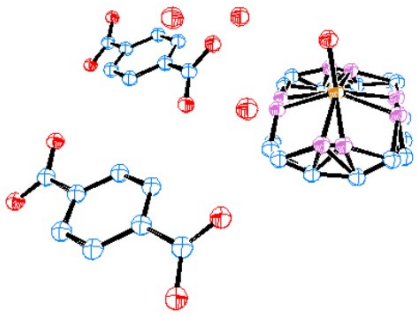
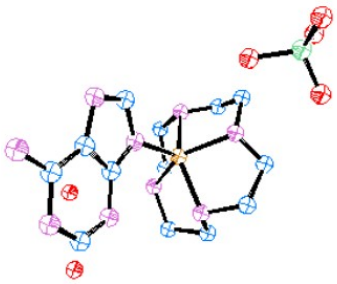
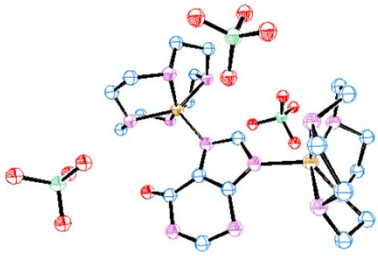
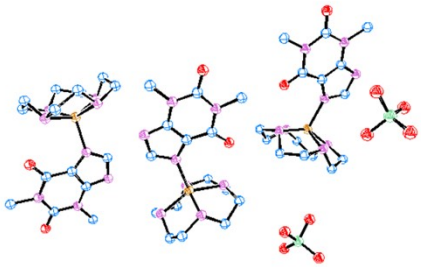
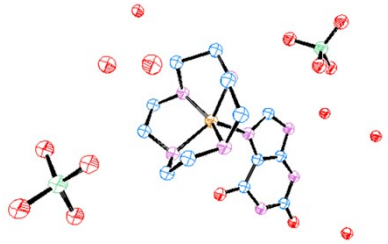
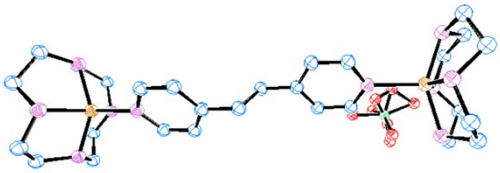
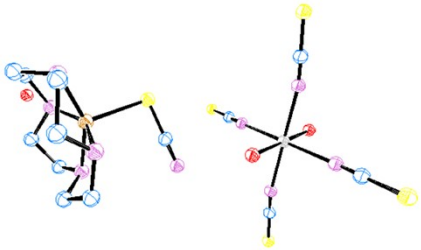
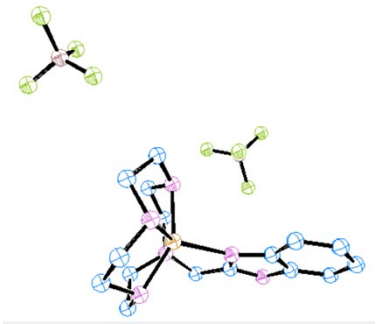
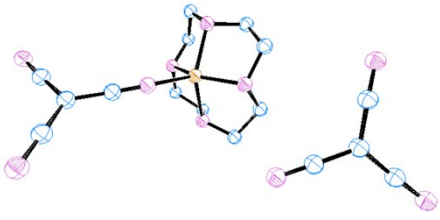
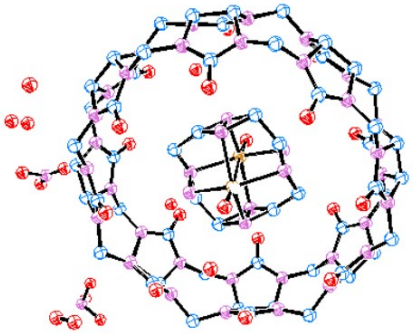
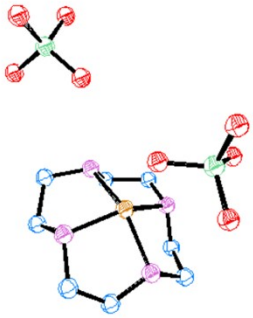
	$[Ni_2(cyclen)_2(tp)](ClO_4)_2$ [S2]			
	 $[Ni_2(trpn)_2(tp)(H_2O)_2](ClO_4)_2$ [S2]	2.07-2.12	8.231	37.424
	 $[Ni_2(3,3,3\text{-tet})_2(tp)(H_2O)_2](ClO_4)_2 \cdot 2H2O$ [S2]	2.09-2.14	9.113	36.223
	 $[(cyclenNi)_2PdL_2]^{2+}$ [S3]	2.09-2.11	10.313	38.318
	 $[Ru^{IV}_4Ni^{II}_2(\mu^3\text{-}OMe)_2(\mu\text{-}OMe)_2(\mu\text{-}N)_2(\mu\text{-}N_3)_2(\mu\text{-}Ophenoxy)_2(sap)_4(MeOH)_4] \cdot 8MeOH$ [S3]	2.10-2.13	7.664	39.359

Table S4. Selected distances and dihedral angle of cyclen in reported Cu(II) complexes with cyclen.			
S.No.	**Complex**	**Cu-Ncy (Å)**	**Dihedral angle (°)**

1.	 [(cyclen)$CuMoO_4]_2(H_2O)_2$[S4]	2.03-2.04	1.213
2.	 [Cu(cyclen)(CH_3CN)][W_6O_{19}][S5]	2.00-2.04	0.929
3.	 [Cu(cyclen)(H_2O)]$(SO)_4 2(H_2O)$[S6]	2.02-2.03	0.245
4.	 [Cu(cyclen)(H_2O)]$(SO)_4(H_2O)$[S6]	2.01-2.03	1.481
5.	 [$Cu(C_8H_{16}N_4O_2)_2$].2(ClO_4) [S7]	2.03-2.08	1.991
6.	 [Cu(cyclen)($N(CN)_2$)]$(N(CN)_2)$ [S7]	1.90-2.04	2.809

7.	 [Cu(cyclen)(CN)$_2$(N(CN)$_4$)] [S7]	1.98-2.03	2.422
8.	 [Cu(Cyclen)H_2O](Tpa)·3H_2O [S8] Tpa = Dianion of Terephalic Acid)	2.00-2.07	2.597
9.	 [Cu(cyclen)(adeninato)] ·ClO_4·2H_2O [S8]	2.02-2.06	3.725
10.	 [{Cu(cyclen)}$_2$(hypoxanthinato)] · $(ClO_4)_3$[S8]	2.00-2.04 2.01-2.08	0.006 0.150
11.	 [Cu(cyclen)(theophyllinato)]$_3$· $(ClO_4)_3$·2H_2O[S8]	2.01-2.07 2.03-2.06	1.900 0.640

12.	 $[Cu(cyclen)(xanthinato)]\cdot(0.7ClO_4)\cdot(0.3ClO_4)\cdot 3H_2O\cdot(0.5H_2O)_3$[S8]	2.01-2.07	3.625
13.	 $[Cu(cyclen)(4,4`\text{-bipy})](ClO_4)_2$[S9]	2.02-2.03 2.02-2.04	0.305 0.548
14.	 $[Cu(SCN)(C_8H_{20}N_4)]^{2-}\,[Ca(NCS)_4(H_2O)_2]\cdot 2H_2O$[S10]	2.02-2.05	0.359
15.	 $CuL^1](BF_4)_2$ [S11] L^1=1-(benzimidazol-2-ylmethyl)-1,4,7,10-tetraazacy-clododecane	2.00-2.08	3.451
16.	 $[Cu(Cyclen)(NO_3)]NO_3$[S12]	2.00-2.03	1.723
17.	 $[Cu(C_4N_3)(C_8H_{20}N_4)](C_4N_3)$[S13]	2.01-2.30	0.023

18.	 $[Cu(Cyclen)(H_2O)]^{2+}[CB_n]$[S14] CB= Cucurbit-[n] uril ; n = 5, 7, and 8	2.06-2.07	0.274
19.	 $[Cu(cyclen)](ClO_4)_2$ [S15]	2.01-2.02	1.474

Reference:

[S1] Yeung, W.; Kwong, H.; Lau, T.; Gao, S.; Szeto, L.; Wong, W. Cyano-Bridged Molecular Squares: Synthesis and Structures of $[Ni(Cyclen)]_2[Pt(CN)_4]_2{\cdot}6H_2O$, $[Ni(Cyclen)]_2[Ni(CN)_4]_2{\cdot}6H_2O$ and $[Mn(Cyclen)]_2[Ni(CN)_4]_2{\cdot}6H_2O$. *Polyhedron* **2006**, *25* (5), 1256-1262.

[S2] Massoud, S.; Mautner, F.; Vicente, R.; Rodrigue, B. Dinuclear Terephthalato-Bridged Nickel(II) Complexes. Structural Characterization and Magnetic Properties. *Inorg. Chim. Acta* **2006**, *359* (10), 3321-3329.

[S3] Xiang, J.; Jia, L.; Man, W.; Qian, K.; Lee, G.; Peng, S.; Yiu, S.; Gao, S.; Lau, T. A Novel Triazidoruthenium (III) Building Block for the Construction of Polynuclear Compounds. *Dalton Trans.* **2012**, *41* (19), 5794.

[S4] Rohde, D.; Merzweiler, K. (1,4,7,10-Tetraazacyclododecane-K^4N^1,N^4,N^7,N^{10}) (Tetraoxidomolybdato-Ko) Copper(II) Monohydrate. *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2010**, *66* (8), 894-894.

[S5] Sarma, M.; Chatterjee, T.; Das, S. A Copper–Cyclen Coordination Complex Associated with a Polyoxometalate Anion: Synthesis, Crystal Structure and Electrochemistry of $[Cu(Cyclen)(MeCN)][W_6O_{19}]$. *Inorg. Chem. Commun.* **2010**, *13* (10), 1114-1117.

[S6] Pérez-Toro, I.; Domínguez-Martín, A.; Choquesillo-Lazarte, D.; Vílchez-Rodríguez, E.; González-Pérez, J.; Castiñeiras, A.; Niclós-Gutiérrez, J. Lights And Shadows in the Challenge of Binding Acyclovir, A Synthetic Purine-Like Nucleoside with Antiviral Activity, At an Apical–Distal Coordination Site In Copper(II)-Polyamine Chelates. *J. Inorg. Biochem.* **2015**, *148*, 84-92.

[S7] Kong, D.; Ouyang, X.; Martell, A.; Clearfield, A. Novel Dioxotetrazamacrocyclic "Sandwich" Complexes – Synthesis and Structural Characterization. *Inorg. Chem. Commun.* **2003**, *6* (3), 317-321.

[S8] Ren, Y.; Li, J.; Zhao, S.; Zhang, F. Synthesis, Crystal Structures And Thermal Decomposition of Two Novel Supramolecular Complexes $[Ni(Cyclen)(H_2O)_2]$ (Tpa) and $[Cu(Cyclen)H_2O](Tpa){\cdot}3H_2O$ (Cyclen = 1,4,7,10–Tetraazacyclododecane, Tpa = Dianion of Terephalic Acid). *Struct. Chem.* **2005**, *16* (4), 439-444.

[S19] Massoud, S.; Druel, E.; Dufort, M.; Lalancette, R.; Kitchen, J.; Grebowicz, J.; Vicente, R.; Mukhopadhyay, U.; Bernal, I.; Mautner, F. Versatile Binding Properties of Di-Pyridyl Ligands with Cu(II) Complexes: The Syntheses, Structural Characterization and Thermal Analysis of Six New Species. *Polyhedron* **2009**, *28* (17), 3849-3857.

[S10] Lu, T.; Lin, J.; Lan, W.; Chung, C. Bis[(1,4,7,10-Tetraazacyclododecane-K_4N) (Thiocyanato-S) Copper(II)] Diaquatetrakis (Isothiocyanato-N) Calcate(2–) Dihydrate. *Acta Crystallogr. Sect. C: Cryst. Struct. Commun.* **1997**, *53* (11), 1598-1600.

[S11] Majzoub, A.; Cadiou, C.; Déchamps-Olivier, I.; Chuburu, F.; Aplincourt, M.; Tinant, B. Mono- And Bis-N-Functionalised Cyclen with Benzimidazolylmethyl Pendant Arms: Sensitive and Selective Fluorescent Probes for Zinc and Copper Ions. *Inorg. Chim. Acta* **2009**, *362* (4), 1169-1178.

[S12] Clay, R.; Murray-Rust, P.; Murray-Rust, J. Nitrato(1,4,7,10-Tetraazacyclododecane) Copper(II) Nitrate. *Acta Crystallogr. Sect. B: Struct. Crystallogr. Cryst. Chem.* **1979**, *35* (8), 1894-1895.

[S13] Luo, J.; Zhang, X.; Qiu, L.; Yang, F.; Liu, B. Crystal Structures of (1,4,7,10-Tetraazacyclododecane-K^4N) Bis (Tricyanomethanido-KN) Nickel and (1,4,7,10-Tetraazacyclododecane-K^4N) (Tricyanomethanido-KN) Copper Tricyanomethanide. *Acta Crystallogr. Sect. E: Cryst. Commun.* **2015**, *71* (6), 693-697.\

[S14] Kim, S.; Jung, I.; Lee, E.; Kim, J.; Sakamoto, S.; Yamaguchi, K.; Kim, K. Macrocycles Within Macrocycles: Cyclen, Cyclam, and their Transition Metal Complexes Encapsulated In Cucurbit [8] Uril. *Angew. Chem., Int. Ed.* **2001**, *40* (11), 2119-2121.

[S15] Gray, J.; Gerlach, D.; Papish, E. Crystal Structure Of (Perchlorato-Ko)(1,4,7,10-Tetraazacyclododecane-K4n)Copper(II) Perchlorate. *Acta Crystallogr. Sect. E: Cryst. Commun.* **2017**, *73* (1), 31-34.