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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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Abstract : Serendipitous self-assembly is a potential approach in achieving structurally versatile and unexpected solids with chosen metal-ligand combinations. Cyclen (1,4,7,10-tetraazacyclododecane) is an interesting flexible molecule, well explored for biological and material applications of its metal complexes. The dihedral angle (θ) between four nitrogen atoms of free cyclen is close to 0°. Still, it may vary upon complexation, allowing flexibility to adopt any two conformers, viz., (i) planar and (ii) twisted. The present work establishes the crucial role of metal ion in controlling the conformation adopted by cyclen through metal complexation. SCXRD studies of complexes of cyclen with Cu^{II} and Ni^{II} with halides and pseudohalides as counter ions reveal the existence of a planar conformation ($\theta = \sim 0-3^\circ$) for cyclen in Cu^{II} systems and a highly twisted conformation (hitherto unreported) in Ni^{II} systems ($\theta = \sim 52-55^\circ$). Further, SQUID magnetic studies for the dimeric [Ni₂] complex reveal antiferromagnetic interactions between the two Ni centres.

1. INTRODUCTION

Serendipitous self-assembly of metal ions' with diverse types of chosen ligands is a potential approach in supramolecular coordination chemistry to derive structurally versatile solids. [1,2] Such an approach, under the influence of structure directing factors, has the potential to generate interesting structures of material relevance. [3] The approach gains more prominence when the ligands are flexible and/or auxiliary anions have diverse binding modes.

Cyclen (1,4,7,10-tetraazacyclododecane) is an interesting flexible molecule, extensively explored for biological and material applications of its metal complexes,[4,5] since long. Being flexible, cyclen can adopt several conformations (Chart 1) ranging from planar to non-planar, depending on the complexation environments. Literature reported Cu and Ni metal complexes of cyclen (Chart 2) have been found to display, two conformations for cyclen, viz., a planar conformation for d^9 configurations of the Cu(II) ion and the twisted conformer as the major one for d^8 configurations of the Ni(II) ions. Early literature studies account for the favourable conformers of cyclen when all the ligand nitrogens' are in the basal plane, for differing coordination geometries of the metal complexes, without regard to the electronic configuration of the metal ions'. [5c-d,6,7] Interestingly, we have not come across such studies when ligand nitrogen's are not necessarily in the basal plane.

Early studies by Busch et al, [5c] focus on the **planar conformation** (a of chart 1) of cyclen and report the optimum M-N distances for metal ions' sitting in the *planar macrocyclic cavity*. Boeyens and Hancock et al, [5d] summarize the optimal M-N distances for metal complexes under different coordination geometries, with ligand nitrogens forming the basal plane that minimize repulsions, resulting in preferred conformations of the tetraaza macrocycles. According to Hancock et al, the ++++ conformer is the favoured conformer for square planar and square pyramidal geometries, while +++- (b of chart 1) conformer is the favourable conformer in octahedral geometry for cyclen in which the cyclic nitrogens form the basal plane.

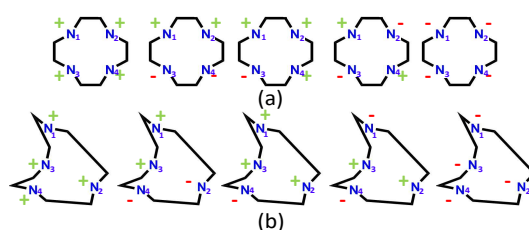


Chart 1. Possible conformations of coordinated tetraaza macrocycle (cyclen) when (a) planar and (b) twisted. The + indicates that the hydrogen of the NH group is above the plane of the flattened macrocycle, while the - indicates that it is below.

Continuing with our interest in synthesizing new molecules with a focus on their magnetic behaviour, our attempts with Ni^{II} , Cu^{II} , cyclen and various linkers based on halides and pseudo halides have resulted in complexes (**[Ni1]-[Ni4]** & **[Cu1]-[Cu4]**) having distinctly different conformations for cyclen. The observed conformations, i.e. planar (in **[Cu1]-[Cu4]**) and twisted (in **[Ni1]-[Ni4]**), have been understood to be due to the change in the dihedral angle of the ring nitrogens (N1 to N4) resulting

from metal complexation. Interestingly, the dihedral angle ($\sim 52\text{--}55^\circ$) between the ligand nitrogens' of cyclen in the series of Ni^{II} complexes leading to the observed twisted conformation is the highest reported till date. The paper gives details regarding synthesis, structure and spectral studies for all the complexes. Further, SQUID magnetic studies for the dimeric **[Ni1]** complex reveal antiferromagnetic interactions between the two Ni centres.

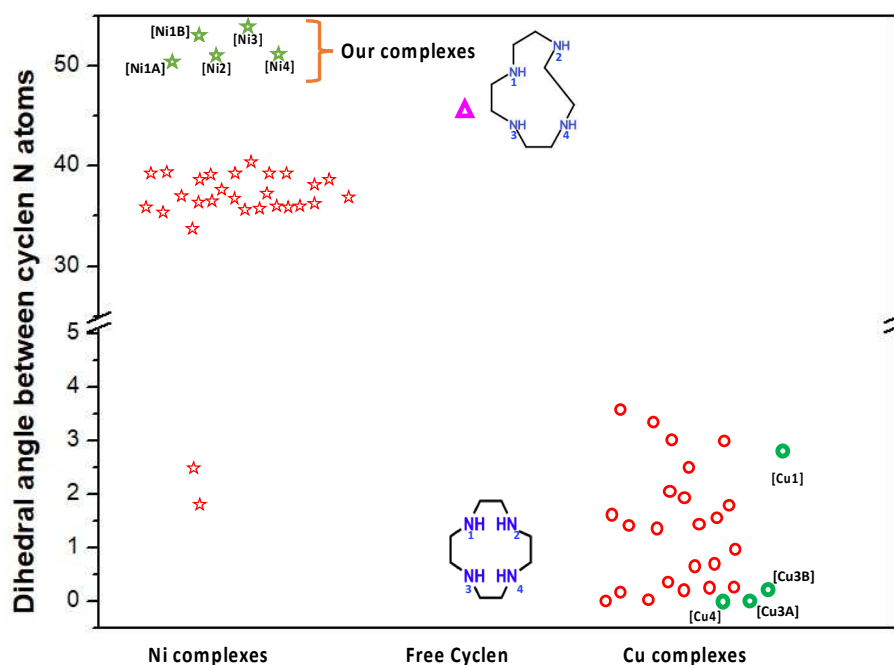


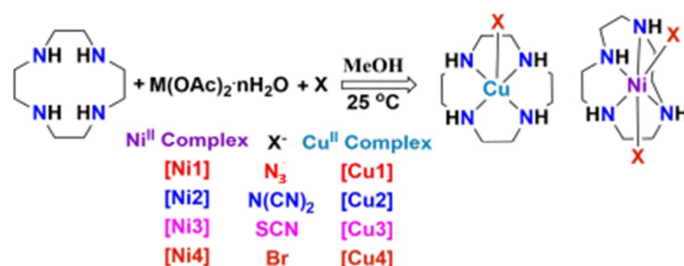
Chart 2. Graphical presentation of the variation of dihedral angle between the cyclen nitrogens in reported Cu^{II} & Ni^{II} complexes, based on CSD search (version 5.38, 01-03-2019) using the search question “*complexes of cyclen with transition metals*” without any filters applied. Green circles and stars correspond to the systems reported in this work while red circles and stars are literature reported systems.

2. EXPERIMENTAL SECTION

2.1 Material and methods: Cyclen, $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, $\text{Cu}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ were purchased from TCI chemicals, whereas NaN_3 , KSCN , $\text{NaN}(\text{CN})_2$ & KBr were procured from Sigma Aldrich and used without further purification. Perkin Elmer Spectrum-2 FTIR spectrometer was employed for FT-IR data collection as KBr pellets in the region 4000 to 400 cm^{-1} . CHN analysis were performed on an Exeter analytical Inc. model: CE 440 elemental analyzer. A BRUKER Quest X-ray (fixed-Chi geometry) diffractometer $\text{Mo-K}\alpha$ radiation ($K\alpha = 0.71073\text{ \AA}$) was employed for single crystal X-ray data collection for complexes **[Ni1]**–**[Ni4]** at 110 K ; PANalytical XRD equipped with Rigaku two circle diffractometer using $\text{Mo-K}\alpha$ radiation at 300 K for **[Cu1]** and a Bruker Kappa APEX-II CCD using D8 X-ray generator, Cryoflex (model Tr-60) $\text{Mo-K}\alpha$ radiation at 300 K for **[Cu3]** and **[Cu4]**. Powder X-ray diffraction (PXRD) data were recorded and collected on a Rigaku Smartlab powder type diffractometer with $\text{Cu K}\alpha 1$ ($\lambda = 1.5406\text{ \AA}$; power 1600 W , 40 kV , 40 mA) at a scan speed of five degrees per minute. The magnetic measurement for **[Ni1]** was carried out with an MPMS-5 QUANTUM DESIGN SQUID magnetometer between 300 and 2 K with an applied field of 1 kOe . Data have been corrected for sample holder and

for the diamagnetic contribution of all atoms by using Pascal's tables.^[8a] The isothermal field dependence of the magnetization was recorded up to 50 kOe. Modelling was performed using PHI.^[8b]

2.2 Preparation of complexes [Ni1] – [Ni4] & [Cu1] – [Cu4]: To a methanolic solution (~ 15 ml) of cyclen (0.10 g, 0.58 mmol), Ni(CH₃COO)₂•4H₂O (0.15 g, 0.58 mmol) was added for the preparation of complexes [Ni1]-[Ni4] and Cu(CH₃COO)₂•2H₂O (0.16 g, 0.58 mmol) for complexes [Cu1]-[Cu4]. After stirring for 10 minutes, NaN₃ (0.06 g, 1.16 mmol), or KSCN (0.08 g, 1.16 mmol), or NaN(CN)₂ (0.08 g, 1.16 mmol) or KBr (0.12 g, 1.16 mmol) was respectively added for the preparation of corresponding complexes. The reaction mixture was stirred overnight at room temperature (25 °C). The clear mother liquor was filtered into a small test tube, which is placed inside a bigger stoppered test tube partially filled with ether. Slow diffusion of ether into the inner tube maintained at 18 °C, afforded single crystals suitable for x-ray structural studies. Suitable single crystals were obtained within 2 days in case of Ni^{II} complexes and one week for Cu^{II} complexes. Yield: [Ni1] = 0.23 g (76.6 %, 0.47 mmol), M.P. 214 (±1)°C. Anal. Calcd. for C₁₆H₄₀N₁₄Ni₂ (MW = 546.04): C, 35.20; H, 7.38; N, 35.92. Found: C, 34.92; H, 7.41; N, 35.42. [Ni2] = 0.28 g (87.5 %, 0.77 mmol), M.P. 209(±1)°C. Anal. Calcd. for C₁₂H₂₀N₁₀Ni (MW = 363.09): C, 39.70; H, 5.55; N, 38.58. Found: C, 39.43; H, 5.34; N, 38.83. [Ni3] = 0.26 g (81.2 %, 0.74 mmol), M.P. 212(±1)°C. Anal. Calcd. for C₁₀H₂₀N₆S₂Ni (MW = 347.15): C, 34.60; H, 5.81; N, 24.21. Found: C, 35.02; H, 5.25; N, 23.94. [Ni4] = 0.32 g (91.6 %, 0.84 mmol), M.P. 182(±1)°C. Anal. Calcd. for C₁₀H₂₃N₄O₂BrNi (MW = 369.94): C, 32.47; H, 6.27; N, 15.15. Found: C, 32.24 ; H, 5.92; N, 15.24. [Cu1] = 0.30 g (93.7 %, 0.79 mmol), M.P. 235(±1)°C. Anal. Calcd. for C₈H₂₀N₁₀Cu (MW = 319.88): C, 41.82; H, 7.02; N, 31.04. Found: C, 41.43; H, 7.23; N, 31.35. [Cu2] = 0.31 g (91.2 %, 0.86 mmol), M.P. 215(±1)°C. [Cu3] = 0.28 g (82.3 %, 0.79 mmol), M.P. 230(±1)°C. Anal. Calcd. for C₁₀H₂₀N₆S₂Cu (MW = 351.98): C, 34.12; H, 5.73; N, 23.88. Found: C, 33.93; H, 5.34; N, 23.90 . and [Cu4] = 0.32 g (84.2 %, 0.81 mmol) M.P. 201(±1)°C. Anal. Calcd. for C₈H₂₀N₄Br₂Cu (MW = 395.64): C, 24.29; H, 5.10; N, 14.16. Found: C, 24.01; H, 4.94; N, 14.31. Procedure for the preparation of complexes is presented schematically in Scheme 1. All the complexes were completely characterized by FT-IR, CHN, PXRD, in addition to SCXRD. Due to poor quality of crystals, SCXRD data for [Cu2] could not be collected.



Scheme 1. Schematic representation for the preparation of complexes. M = Ni^{II} for [Ni1]-[Ni4] and M = Cu^{II} for [Cu1]-[Cu4] whereas X = N₃⁻, N(CN)₂⁻, SCN⁻ and Br⁻ respectively.

2.3 Crystallographic data collection and refinement: Data collection was done for the title complexes as detailed in sec. 2.1. Hydrogen atoms were set as riding on the parent atoms after placing them in idealized positions around respective parent atoms. Atoms were refined with anisotropic thermal parameters except for the hydrogen atoms. The absence of additional symmetry and voids were confirmed using PLATON (ADDSYM).^[9] The structures were solved by direct methods and refined by full-matrix least-squares on F² using the latest version of SHELX-2018.^[10] The refinement converged to final values of R1 & wR2 = 0.0587 & 0.1399 for [Ni1]; 0.0485 & 0.1524 for

Table 1. Important Crystal Data for title Complexes.

Complex	[Ni1]	[Ni2]	[Ni3]	[Ni4]	[Cu1]	[Cu3]	[Cu4]
Empirical formula	C ₁₆ H ₄₀ N ₁₄ Ni ₂	C ₁₂ H ₂₀ N ₁₀ Ni	C ₁₀ H ₂₀ N ₆ S ₂ Ni	C ₁₀ H ₂₃ BrN ₄ O ₂ Ni	C ₈ H ₂₀ N ₁₀ Cu	C ₁₀ H ₂₀ N ₆ S ₂ Cu	C ₈ H ₂₀ Br ₂ N ₄ Cu
CCDC No.	1889902	1889904	1889951	1889905	1890811	1890876	1890877
F.W.	546.04	363.09	347.15	369.94	319.88	351.98	395.64
Space group	C2/m	Pbca	R ₃ c	Pnma	P2 ₁ /n	P2 ₁ 2 ₁ 2 ₁	P4/nmm
Crystal system	Monoclinic	Orthorhombic	Trigonal	Orthorhombic	Monoclinic	Orthorhombic	Tetragonal
a (Å)	13.2618(9)	12.8420(6)	22.9171(16)	15.1276(11)	8.3568(4)	12.8292(9)	9.5813(6)
b (Å)	8.7178(6)	14.8998(6)	22.9171(16)	8.9116(7)	14.4655(7)	13.3387(10)	9.5813(6)
c (Å)	13.2822(9)	16.5728(7)	15.2853(11)	11.1889(8)	11.2207(5)	18.2848(14)	7.5171(5)
α, β, γ (°)	90,109.205(2), 90	90, 90, 90	90, 90,120	90, 90, 90	90,92.84(12), 90	90, 90, 90	90, 90, 90
V (Å ³)	1450.14(17)	3171.1(2)	6952.2(11)	1508.39(19)	1354.74(11)	3129.0(4)	690.08(10)
T (K)	110.0	110.0	110.0	110.0	273	110	300
Z	2	8	18	4	4	8	2
D _{calc} (mg m ⁻³)	1.251	1.521	1.492	1.629	1.568	1.494	1.904
μ (mm ⁻¹)	1.327	1.240	1.522	3.936	1.618	1.659	7.351
GOF on F ²	1.115	1.079	1.068	1.182	1.076	1.007	1.064
R (F _o ²) ^a	0.0587	0.0485	0.0486	0.0434	0.0220	0.0616	0.0288
Rw (F _o ²) ^b	0.1399	0.1524	0.1178	0.0814	0.0525	0.0683	0.0327
^a R ₁ = Σ F _o - F _c / Σ F _o . ^b wR ₂ = [Σ[w(F _o ² - F _c ²) ²] / Σ[w (F _o ²) ^{3/2}] ^{1/2}							

[Ni2]; 0.0486 & 0.1178 for [Ni3]; 0.0434 & 0.0814 for [Ni4]; 0.0220 & 0.0525 for [Cu1]; 0.0616 & 0.0683 for [Cu3] and 0.0288 & 0.0327 for [Cu4] respectively. Important crystal data are presented in Table 1 and bond length and angles in ESI Table S1. Drawings are made using OLEX-II,^[11] and MERCURY.^[12]

3. RESULTS AND DISCUSSION

3.1 Synthesis and vibrational spectroscopic studies.

A series of Ni^{II} and Cu^{II} complexes have been synthesized in-situ in a step-wise manner with reasonable yields. Complexes are blue blocks with sharp melting points. The PXRD patterns (ESI, Figure S1) confirm the bulk purity of the products, as can be seen from the agreement of the experimental PXRD patterns with the simulated patterns, indicating that the crystal structures are true representatives of the bulk products.

All the complexes exhibit strong and sharp vibrational bands at 3000 - 3300 cm⁻¹ in FT-IR (ESI, Figure S2), which corresponds to the N-H symmetric and asymmetric stretching of the core moiety (cyclen) containing four N-H bonds.^[13] There are other sharp bands appearing at 1455 cm⁻¹ (m), 968 cm⁻¹, (s) 883 cm⁻¹ (s) and one broad band at about 1630 cm⁻¹ (s) corresponding to the characteristic (C-H) bands for the core moiety. Due to the presence of N₃⁻ group, sharp bands at 2127 cm⁻¹ (s) and 2182 cm⁻¹ (s) corresponding to asymmetric $\mu_{1,3}$ and end-on stretching modes of azide are observed for the complexes [Ni1] & [Cu1] respectively.^[14] Symmetric and asymmetric end on stretching vibrations of N(CN)₂⁻ have been observed at 2140 cm⁻¹ (m) & 2225 cm⁻¹ (m) for [Ni2] and at 2127 cm⁻¹ (m) and 2182 cm⁻¹ (m) for [Cu2]. [Ni3] shows sharp band at 2035 (s) corresponding to symmetric end-on stretching of NCS⁻ group. Sharp bands at 2144 cm⁻¹ (s) correspond to end-on symmetric stretching of coordinated SCN⁻, and bands at 2251 cm⁻¹ (m) and 2287 cm⁻¹ (m) correspond to the asymmetric stretching vibrations of uncoordinated SCN⁻ of [Cu3]. The fingerprint region in all the complexes shows sharp bands at 526 cm⁻¹ and 421 cm⁻¹ corresponding to the Ni-N and Cu-N stretching frequencies respectively. The rest of the spectral patterns and band positions of all the complexes are very similar and are shown in ESI (Figure S2).

3.2 Single crystal X-ray diffraction structural studies.

3.2.1. [Ni(cyclen)N₃]₂ [Ni1] [diazido(1,4,7,10-tetraazacyclododecan-1-yl)nickel] : Complex [Ni1] crystallizes in the monoclinic space group C2/m. Ni^{II} adopts distorted octahedral geometry, with three cyclen nitrogens (N2, N3, N2¹) occupying the basal plane and the fourth position occupied by azide nitrogen (N6¹). The axial positions of the octahedron are occupied by one of the cyclen nitrogen (N1) and nitrogen of the second azide (N4) (Figure 1a). The M-N distances are in the range 2.03 - 2.12 Å, respectively (Table S1). Ni^{II} is displaced by (d) 0.189 Å from the mean plane of the coordinating nitrogen atoms. The azide group acts as a symmetric μ -1,3 bridge and connects two Ni^{II} centres forming a dimer, where one of the N₃⁻ group orients equatorially while the other tends to be axial. The Ni-N_{az} distances in the [Ni1] dimer are slightly lesser than double μ -1,3 azido bridged Ni^{II} dimers in which azide is in axial – equatorial sites of the coordination polyhedron.^[15] The dihedral angle between the ligand N's in the two-cyclen moieties is 51.8° and 53.3° (Table S2). Intradimer separation between the two Ni^{II} centres (5.313 Å) is much less than the separation observed (ranging

between 7-11 Å) for reported dimeric Ni^{II} complexes of cyclen (ESI Table S3). Neighbouring dimers are non-interacting and are arranged parallel in 3-dimensions, as shown in Figure 1b.

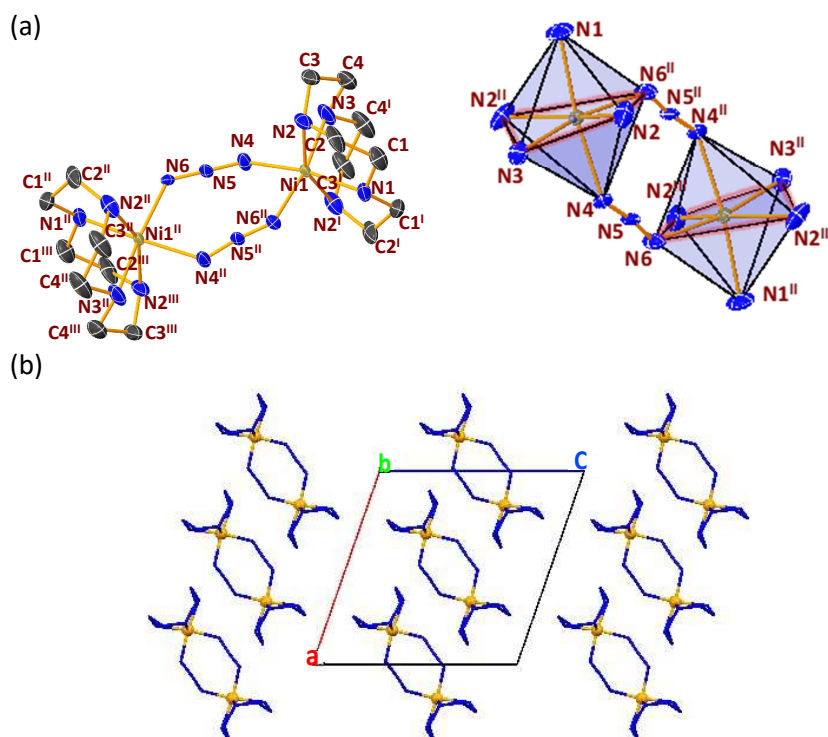


Figure 1. (a) (left) ORTEP of [Ni1] showing atoms as 40 % probability ellipsoids. Ring hydrogens have been omitted for clarity. (right) Corresponding Polyhedral drawing showing the coordination environment around the metal center. (b) Packing of dimers in the unit cell. Symmetry codes: ^I = x, -y, z; ^{II} = 1-x, y, 1-z; ^{III} = 1-x, -y, 1-z.

3.2.2. [Ni(cyclen)(N(CN)₂)₂] [Ni2]: bis(N-cyanocyanamido)(1,4,7,10-tetraazacyclododecan-1-yl)nickel]: Complex [Ni2] crystallizes in orthorhombic space group Pbc_a. Monomeric [Ni2] is in a distorted octahedral geometry with three cyclen nitrogens (N1, N2 & N3) occupying the basal plane and the fourth position occupied by nitrogen of one of the anionic dicyanamide (N5). Axial positions of the octahedron are occupied by one of the cyclen nitrogen (N4) and nitrogen (N8) of the second dicyanamide group (Figure 2a). The coordination polyhedron around Ni^{II} is comparable to previously reported dicyanamide bridged Ni^{II} dimer with cyclen.^[16] The M-N distances are 2.06 – 2.13 Å and 2.107 Å, respectively (Table S1). Ni^{II} deviates by d = 0.167 Å from the mean plane of the coordinating nitrogen atoms. The dihedral angle between the four nitrogen of the ligand is 52.1° (Table S2). Individual monomers act as hydrogen bond donors (through N_{cy}-H) and acceptors (through dicyanamide N's). They are interconnected with weak hydrogen bonding interactions with neighbouring monomers (N1-H1...N10 : 3.023(5) Å; N4-H4...N10 Å : 3.167(5) Å; N3-H3...N7 : 3.046(5) Å; C8-H8B...N7 : 3.590(5) Å) (Figure 2b), leading to a 2-D layer arrangement in the unit cell.

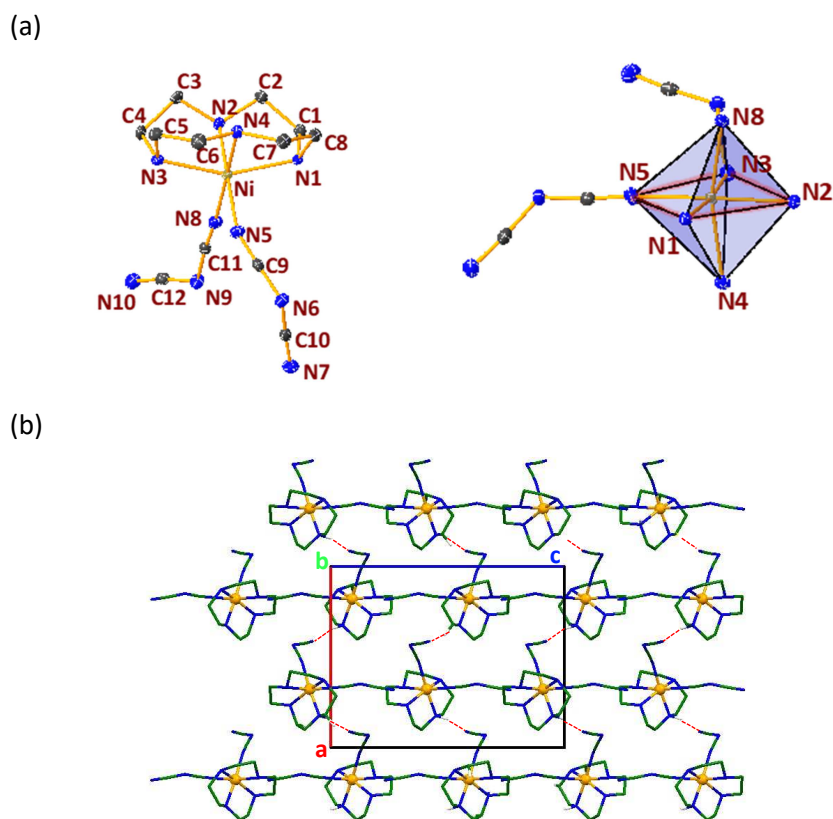


Figure 2. (a) (left) Ortep of $[\text{Ni}2]$ showing atoms as 40 % probability ellipsoids. Ring hydrogens have been omitted for clarity; (right) Coordination polyhedron around the metal center; (b) Packing of hydrogen bonded monomers in the unit cell.

3.2.3. $[\text{Ni}(\text{cyclen})(\text{SCN})_2]$ $[\text{Ni}3]$ [(1,4,7,10-tetraazacyclododecan-1-yl)diisothiocyanatonickel] : Complex $[\text{Ni}3]$ crystallizes in a trigonal crystal system with space group R3c. The asymmetric unit contains one metal centre, one ligand and two thiocyanate anions. Three nitrogen atoms fulfil octahedral geometry of Ni^{II} from the ligand (N1, N2 & N3) and fourth nitrogen (N5) from one of the thiocyanate in the basal plane; the fourth ligand nitrogen (N4) and nitrogen (N6) of the second thiocyanate moiety occupy the axial positions (Figure 3a). The M-N distances are in the range 2.07 – 2.16 Å (Table S1). The dihedral angle between the four nitrogen atoms of the ligand is 54.6° (Table S2). The metal ion deviates by 0.121 Å from the mean plane of the coordinating nitrogens. Terminal sulphur atoms of the coordinated thiocyanate moieties are involved in bifurcated hydrogen bonding interactions with the amino hydrogens of the neighbouring cyclen units (N2-H1...S2 : 3.481(4) Å; N4-H4...S2 : 3.553(4) Å; N1-H1...S2 : 3.620(4) Å; N3-H3...S1 : 3.578(6) Å), giving a trigonal packing of the monomeric units when viewed down the b axis of the unit cell (Figure 3b).

3.2.4. $[\text{Ni}(\text{cyclen})(\text{CH}_3\text{COO})]\text{Br}$ $[\text{Ni}4]$ [(1,4,7,10-tetraazacyclododecan-1-yl)nickel(II) bromide]: $[\text{Ni}4]$ crystallizes in orthorhombic space group Pnma. The asymmetric unit contains one metal ion, half ligand, one acetate group and one bromide ion in the asymmetric unit lying on a symmetry plane. The other half of the ligand is symmetry generated.

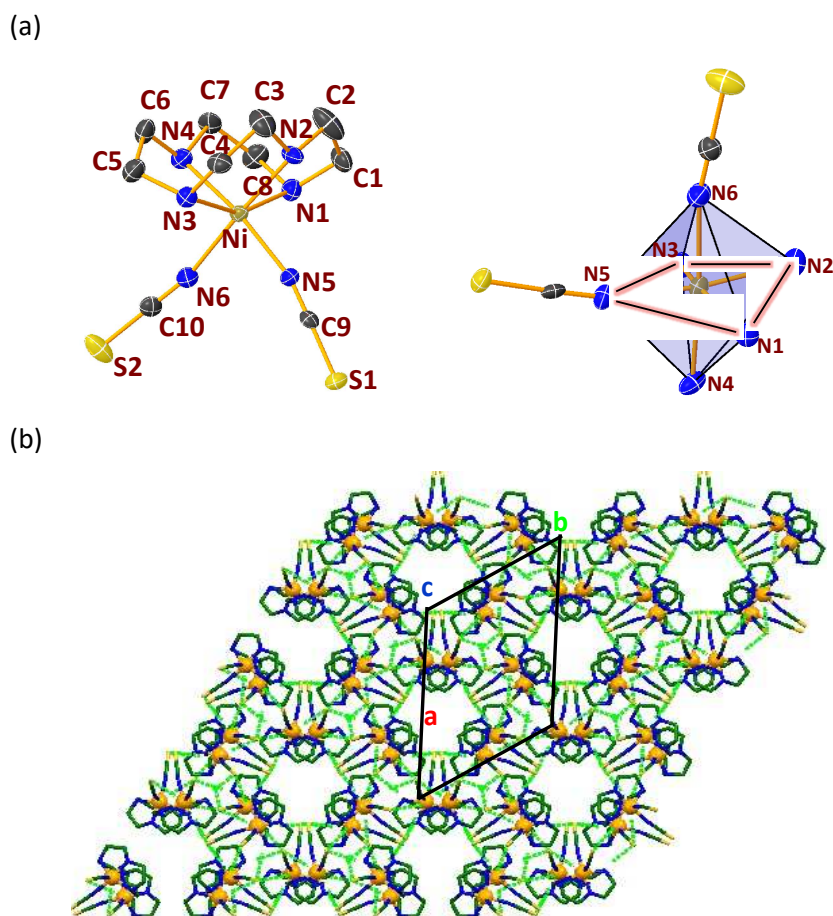


Figure 3. (a) (left) Ortep of $[\text{Ni}3]$ showing atoms as 40 % probability ellipsoids. Ring hydrogens are omitted for clarity; (right) Coordination polyhedron around the metal centre; (b) Packing of monomers in the unit cell.

Though the metal ion adopts octahedral geometry, the equatorial sites are occupied by two nitrogen atoms from the ligand (N1 & N3) and two oxygen (O1 & O2) atoms from acetate group, which defines the mean plane. In contrast, the axial positions are occupied by the other two nitrogen atoms of the ligand (N1 & N4) (Figure 4a). M-N distances are in the range 2.03-2.06 Å (Table S1). Ni^{II} is found to be displaced by 0.142 Å from the basal plane of the coordinating nitrogens. The dihedral angle between the four nitrogen atoms of ligand is found to be 52.6° (Table S2). The uncoordinated bromide ions connect the monomers into a zig-zag chain through hydrogen bonding interactions (N1-H1 \cdots Br1 : 3.346(4) Å), (Figure 4b).

In general, cyclen adopts a twisted conformation in all the structures (Table S2), similar to that observed in other Ni-cyclen complexes with diverse anions (Chart 2). The trends in Ni-N_{cy} bond lengths are similar for all complexes and are in accordance with other reported Ni-cyclen complexes (ESI Table S3). However, the dihedral angle between the cyclen nitrogens (~52-55°) observed here is much higher than the angle (35-40°) in the Ni^{II} complexes of cyclen reported so far (chart 2), thus revealing a new conformational angle and geometry for the twisted conformation of cyclen in Ni^{II} complexes.

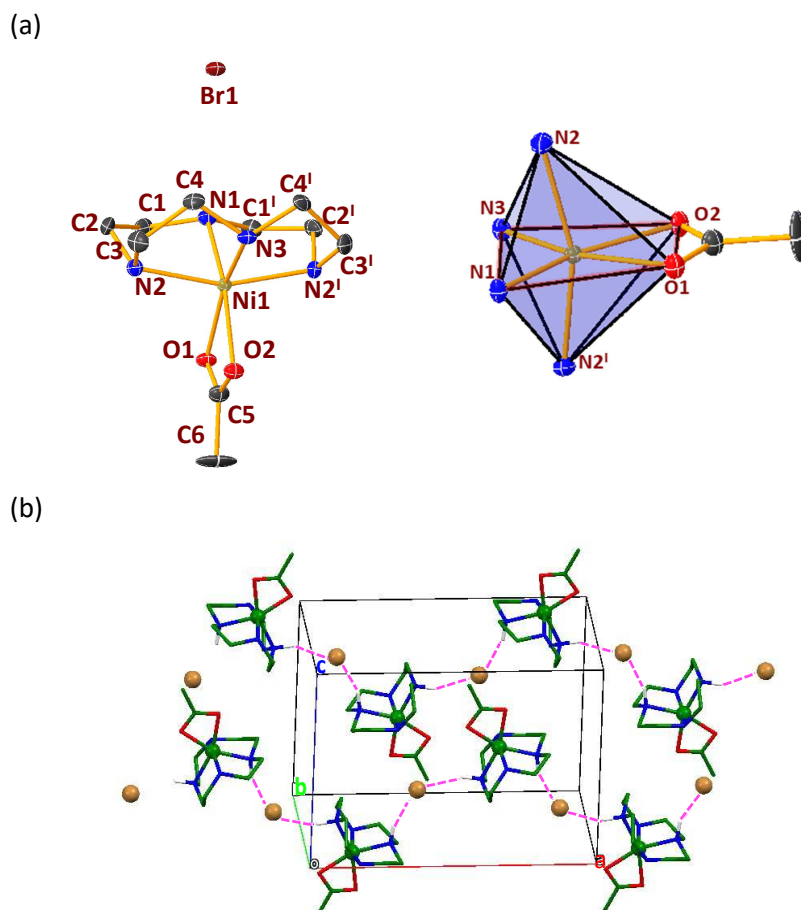


Figure 4. (a) (left) Ortep of $[\text{Ni}4]$ showing atoms as 40 % probability ellipsoids. Ring hydrogens have been omitted for clarity; (right) Coordination polyhedron around the metal center. (b) Hydrogen bonded zig-zag chain of monomers in the unit cell. Symmetry code: $^1 = x, -y, z$.

3.2.5. $[\text{Cu}(\text{cyclen})\text{N}_3]\text{N}_3$ $[\text{Cu}1]$ [azido(1,4,7,10-tetraazacyclododecan-1-yl)copper]: Monomeric $[\text{Cu}1]$ crystallizes in the monoclinic space group $P2_1/n$ with a distorted square pyramidal geometry around the metal centre. The asymmetric unit contains one metal centre, one ligand and two azide moieties. The ligand nitrogens (N1, N2, N3 & N4) occupy the basal plane, and azide nitrogen (N5) of one moiety occupies the pyramidal position (Figure 5a) of the metal ion. Cu-N_{cy} and Cu-N_{az} bond lengths are 2.01-2.04 Å and 2.10 Å, respectively (Table S1). Cu^{II} is displaced by 0.5330(6) Å from the basal plane. The dihedral angle between the four nitrogen atoms of the ligand is found to be 2.7° (Table S2). Both coordinated and uncoordinated azides are involved in hydrogen bonding interactions with the amino hydrogens of the ligand. The coordinated azides connect the symmetry-related monomers into a dimer through amino N_{cy}-H...N_{az} (H...A 1.994 Å) hydrogen bonding interactions (red dashed lines, fig. 5b). The uncoordinated azides not only connect the monomers of the same symmetry into a hydrogen-bonded chain involving amino N-H...N_{az} (N1-H1...N10 : 2.973(18); N3-H3...N8 : 3.052(18) Å) hydrogen bonds but also connect the symmetry-related dimers to neighbouring dimers (N4-H4...N10 : 2.972(17) Å), leading to a 2-D layer (black dashed lines, figure 5b).

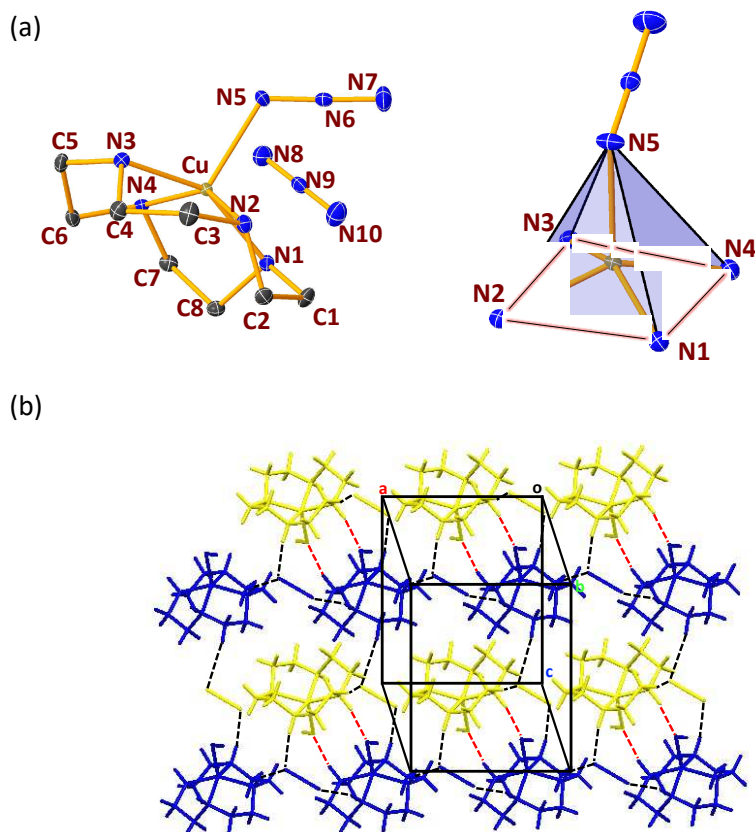


Figure 5. (a) (left) Ortep of **[Cu1]** showing atoms as 40 % probability ellipsoids. Ring hydrogens have been omitted for clarity; (right) Coordination polyhedron around the metal center; (b) Packing of H-bonded dimers into a 2-D layer in the unit cell.

3.2.6. $[\text{Cu}_2(\text{cyclen})_2(\text{SCN})_2][\text{SCN}]_2 [\text{Cu3}]$ [(1,4,7,10-tetraazacyclododecan-1-yl)(isothiocyanato)copper]: Complex **[Cu3]** crystallizes in orthorhombic space group $P2_12_12_1$. The asymmetric unit contains two independent $[\text{Cu}(\text{cyclen})(\text{NCS})]^+$ moieties and two uncoordinated NCS^- units. While the metal ion exhibits square pyramidal geometry, the two units are distinct by the coordination mode of the thiocyanate moiety in the pyramidal position. In the first unit, the distorted square pyramidal geometry is fulfilled by the four nitrogen atoms of the ligand forming the basal plane (N1A, N2A, N3A & N4A), while the fifth axial site is occupied by the S (S1A) of the thiocyanate moiety (Figure 6a). However, in the second unit, the distorted square pyramidal geometry of the metal center is fulfilled by the ligand nitrogens (N1B, N2B, N3B & N4B) and the pyramidal position is occupied by the nitrogen of second thiocyanate moiety, (N5B). Displacement of Cu^{II} from the basal plane is 0.556 Å & 0.589 Å in both units, respectively. The dihedral angle between four nitrogen atoms of the ligand is 0.2 ° and 0.0 ° for the two independent units, respectively (Table S2). The two cyclen units are arranged in a flip-flop manner as pairs connected through hydrogen bond interactions ($\text{N}_{\text{cy}}\text{-H}\cdots\text{N}_{\text{SCN}} = 2.960$ Å) between ring amino hydrogens of the first unit and the N end of the coordinated thiocyanate of the second unit (red dashed lines in figure 6c). The uncoordinated thiocyanate moieties connect the neighbouring flipped pairs into a 2-D layer arrangement in the unit cell through hydrogen-bonding interactions with ring amino hydrogens. ($\text{N4A-H4A}\cdots\text{S1C} : 3.318(5)$ Å; $\text{N1B-H1B}\cdots\text{N1C} : 2.957(8)$ Å; $\text{N3A-H3A}\cdots\text{S1D} : 3.439(6)$; $\text{N3B-H3B}\cdots\text{S1D} : 3.338(5)$ Å, black lines in fig. 6b).

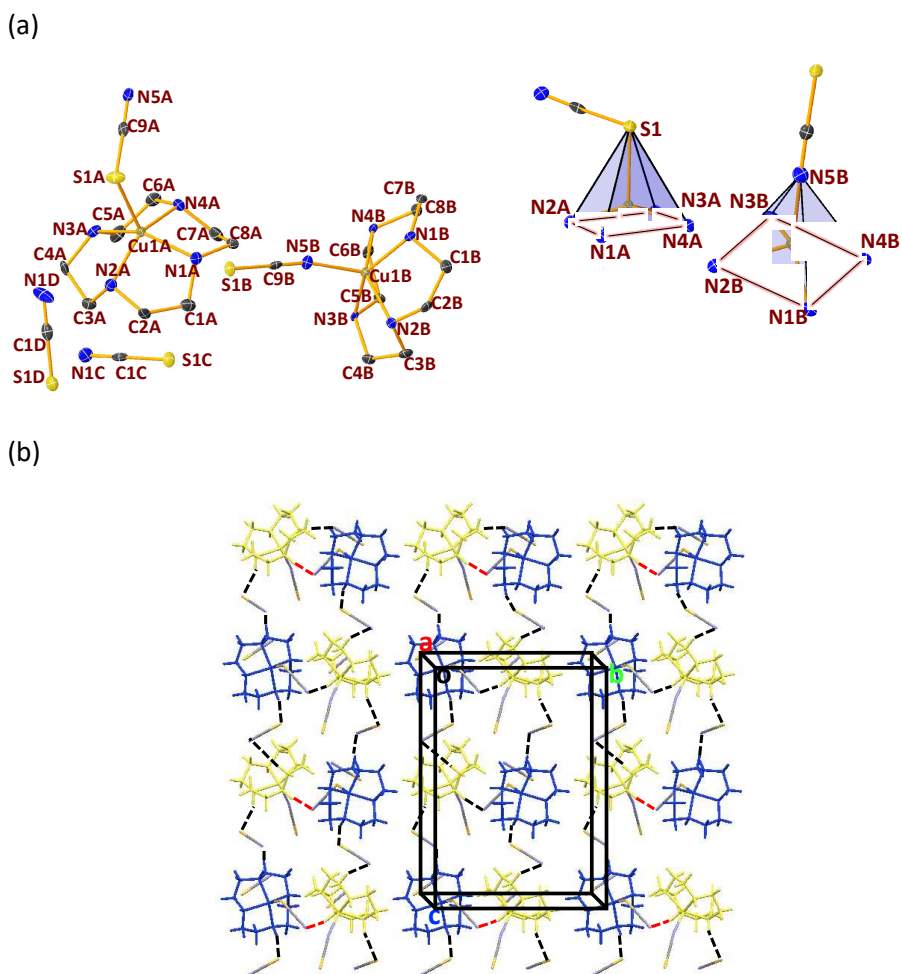


Figure 6. (a) (left) Ortep of $[\text{Cu}_3]$ showing atoms as 40 % probability ellipsoids. Ring hydrogens have been omitted for clarity; (right) Coordination polyhedron around the metal center; (b) 2-D layer arrangement of flipped pairs.

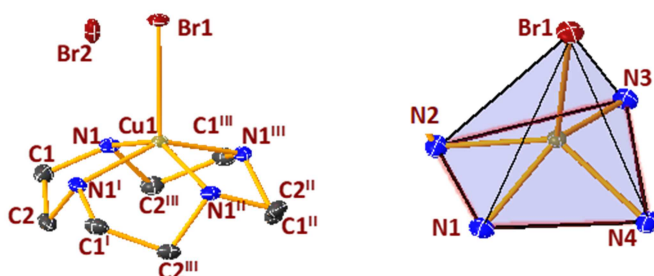
3.2.7. $[\text{Cu}(\text{cyclen})\text{Br}]\text{Br}$ [Cu4] [(1,4,7,10-tetraazacyclododecan-1-yl)copper(II) bromide]: Complex $[\text{Cu4}]$ crystallizes in the tetragonal space group $P4/nmm$ with square pyramidal geometry around the metal center. Nitrogens of ligand occupy the four equatorial positions (N1, N2, N3 & N4), forming the basal plane whereas bromide ion (Br1) occupies the pyramidal position (Figure 7a). The Cu^{II} ion is displaced by $0.593(2)$ Å from the basal plane. The dihedral angle for the four ligand nitrogen atoms is found to be 0.0° (Table S2). In the asymmetric unit, there is another bromide ion (Br2) that is uncoordinated and connects the neighbouring $[\text{Cu}(\text{cyclen})\text{Br}]^+$ units into a 2-D network through hydrogen bonding interactions ($\text{N1-H1}\cdots\text{Br2} = 3.319$ Å) (Figure 7b).

3.3. Structural Comparisons between Ni & Cu Series.

The diverse shapes exhibited by all the metal complexes may be attributed to the conformational flexibility of the ligand to support the metal ions' geometrical preferences arising out of CFSE, supported by the shape of the anion. Cyclen being flexible, when put in solution containing metal ions' and anions, adjusts its conformation to suit the metal ions' geometrical preferences, thereby adopting a twisted conformation with Ni^{II} ion and a planar conformation with Cu^{II} ion, that maximises the CFSE of the respective metal ions. By doing so, it supports the metal complex attain diverse shapes in association with the anion, which may be depicted as a cartoon representation as an azide

bridged dumbbell of **[Ni1]**; Tom Cat of **[Ni2]** with bent dicyanamide; Jerry Mouse of **[Ni3]** with a linear thiocyanate and a wine glass shape of **[Ni4]** with coordinated acetate. (Scheme 2).

(a)



(b)

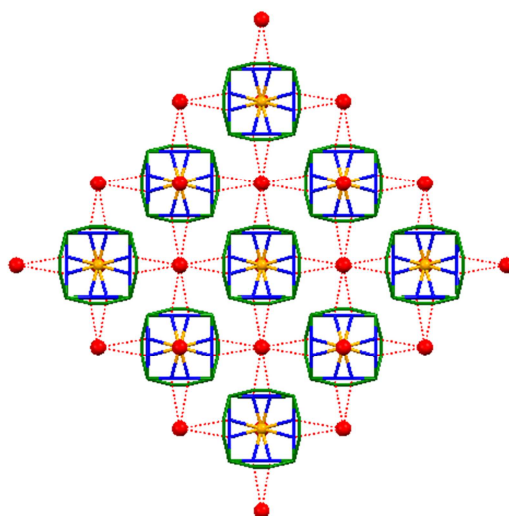
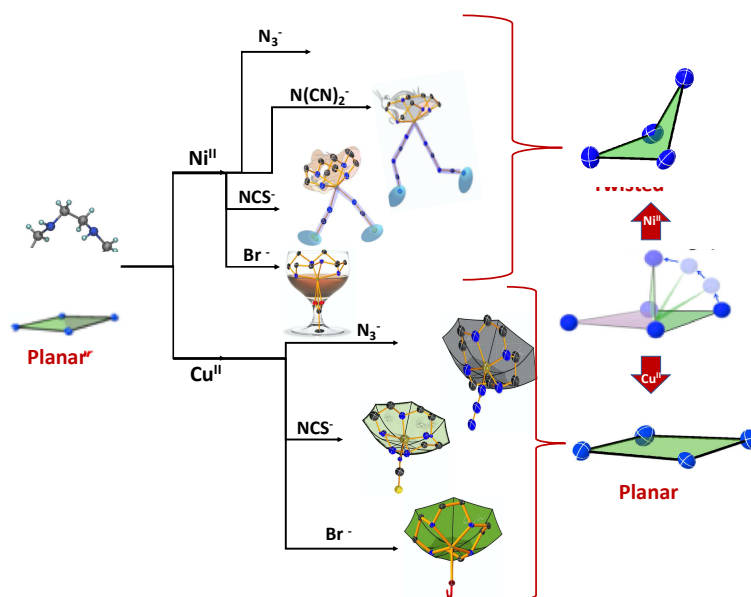


Figure 7. (left) Ortep of **[Cu4]** showing atoms as 40 % probability ellipsoids. Ring hydrogens have been omitted for clarity; (right) Coordination polyhedron around the metal center. (b) Packing of monomers through hydrogen bonding interactions. Symmetry code: ⁱ = x, 3/2-y, z; ⁱⁱ = 3/2-x, 3/2-y, z; ⁱⁱⁱ = 3/2-x, y, z

With a larger twist in the ligand conformation (dihedral angle of ligand nitrogens = ~ 52 - 55°), this anionic effect is more pronounced in the Ni^{II} series. However, with a planar ligand around the Cu(II) ion (dihedral angle of ligand nitrogens = ~ 0 - 3°), the gross shape of the molecule remains the same (an inverted umbrella - cartoon representation) similar to other reported complexes (ESI, Table S4), with a minimal effect of the anion that shows up in the packing patterns only.

The planar conformation (++++) of cyclen in all the copper complexes is in accordance with the predictions of Hancock et al. for square pyramidal geometry.^[6] However, in Ni^{II} complexes, cyclen displays several conformations as ++++ in **Ni1** and **Ni3**; +++- in **Ni2**; and -+++ in **Ni4**, very much different from the predictions (+++-) of Hancock et al for an octahedral geometry of a metal ion, where all the ligand amino nitrogens are in the basal plane. The variations in ligand conformation in our case appears to arise from the difference in planar atoms for the octahedral geometry, where only three amino nitrogens of the ligand are in basal plane and the fourth position is occupied by different anionic atoms.



Scheme 2: Schematic presentation of the diverse shapes arising out of metal ion's coordination supported by anions.

3.4. Magnetic Studies of Ni1.

The magnetic behaviour for the azide-bridged Ni dimer, **[Ni1]** has been investigated in the temperature domain 2 – 300 K. The temperature dependence of $\chi_M T$ (χ_M stands for the molar magnetic susceptibility) for **[Ni1]** is characteristic for strong antiferromagnetic interaction between the two Ni centres (Figure 8a). The value for $\chi_M T$ at 300 K, $1.45 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$, is below the Curie contribution of $2 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ expected for two Ni ($S = 1$, $g = 2.0$) and steadily decrease as T is lowered to reach almost zero below 20 K. The related $\chi_M = f(T)$ shows a broad maximum at 110 K (Figure 8(b)).

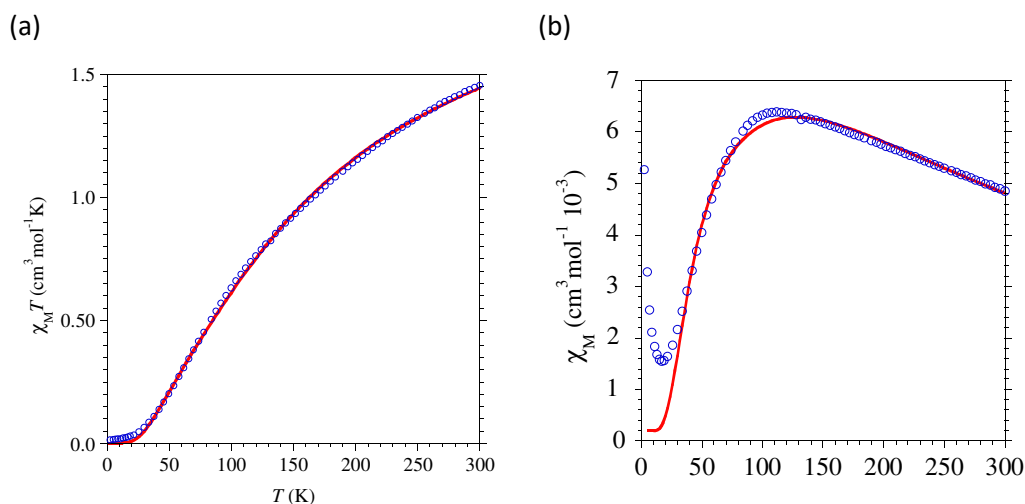


Figure 8: (a) Experimental (O) and calculated (–) temperature dependence of $\chi_M T$ and (b) χ_M for **[Ni1]**

The modelling performed with a dimer model for two $S = 1$ centres (reference Hamiltonian is $\hat{H} = -J(\hat{S}_{Ni1} \cdot \hat{S}_{Ni2})$) lead to an interaction parameter of $J = -82.1 \pm 0.2 \text{ cm}^{-1}$ for $g = 2.0$. The obtained

exchange parameter is in accordance with values reported for related compounds^[15, 16, 17] and confirms the strong Ni-Ni antiferromagnetic interaction mediated by the azido-bridges.

CONCLUSION

Self-assembly of Ni^{II} or Cu^{II} with conformationally flexible cyclen in the presence of pseudohalides has resulted in title complexes which are characterised structurally. All the Ni^{II} complexes display a twisted conformer for the ligand with a large dihedral angle (52-55°, Table S2) between the cyclen nitrogens, *not reported till now*, while the Cu^{II} complexes display a planar conformation, as predicted by Hancock et al. The variation in the cyclen conformers as seen in Ni^{II} complexes (++++ in **Ni1** and **Ni3**; +++- in **Ni2**; and -+++ in **Ni4**) and Cu^{II} (++++) complexes has been explained by the changes in the dihedral angle of the ligand nitrogens. The change in ligand conformation from twisted in Ni^{II} to planar in Cu^{II} complexes has been understood in terms of the metal ions' geometrical preferences imposed by CFSE. The Jahn-Teller effect in Cu^{II} allows the sustenance of planar conformation of cyclen by adopting a square pyramidal geometry where all four N atoms of cyclen complex to Cu^{II} in the square plane and different anions (N₃⁻, SCN⁻ & Br⁻) occupy the pyramidal position resulting in a gross inverted umbrella structure for all the complexes (**[Cu1]**-**[Cu4]**) with no anion effect on the molecular shape. In the absence of J-T distortion, in octahedral Ni^{II} complexes, the ligand is highly distorted (dihedral angle = ~52-55°) to support the octahedral geometry of the metal ion, thus attaining a twisted conformation, in which the ligand nitrogens' occupy three positions of the square plane, and anionic nitrogen occupy the remaining one position, as seen through X-ray structures. Due to the positioning of anionic nitrogens' in the square plane, depending on the anion, different structures were obtained for Ni-cyclen-X complexes, viz., "Dumb bell-shaped structure" with azide **[Ni1]**, "Tom cat structure" with dicyanamide **[Ni2]**, "Jerry mouse structure" with thiocyanate **[Ni3]** and "Wine-Glass structure" with bromide **[Ni4]** ions. The **[Ni1]** dumbbell shows antiferromagnetic interactions ($J = -82.1 \pm 0.2 \text{ cm}^{-1}$) between the end-to-end azide bridged Ni centers.

The present study involving the serendipitous self-assembly approach is successful in providing a new conformation for cyclen with a large dihedral angle (~52-55°), the highest reported so far between its ring nitrogens. The increased dihedral angle of the ligand in its non-planar mode of coordination to support Ni^{II} octahedral geometry, in association with diversely shaped anions, resulted in interesting structures under self-assembling conditions. The examples are important as there are no literature reports predicting the conformations of cyclen for octahedral geometry in which not all its ring nitrogens' form the basal plane. The work provides scope for in-depth theoretical studies in finding out all the possible conformations for cyclen in octahedral coordination when all ligand nitrogens are not necessarily in basal plane of the metal ion. More examples may be helpful in developing functional molecules and study their functionality based on variations in structure.

ACKNOWLEDGEMENTS

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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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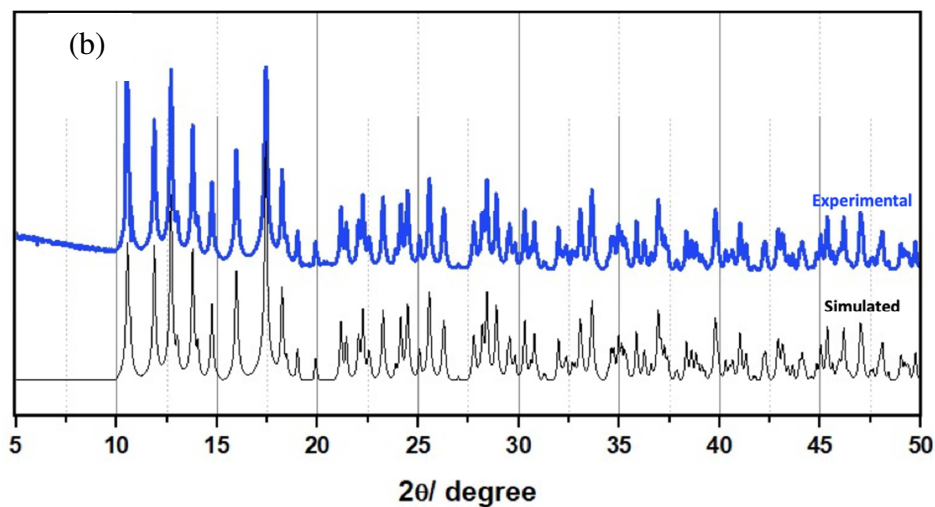
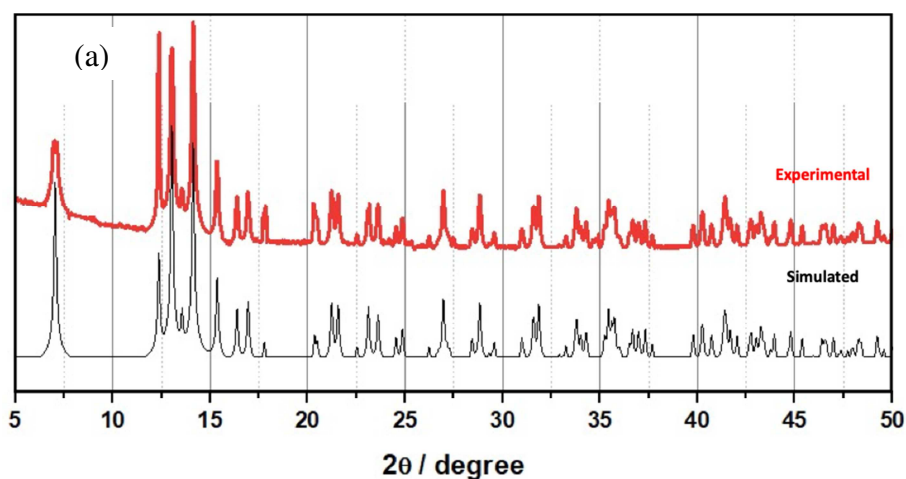
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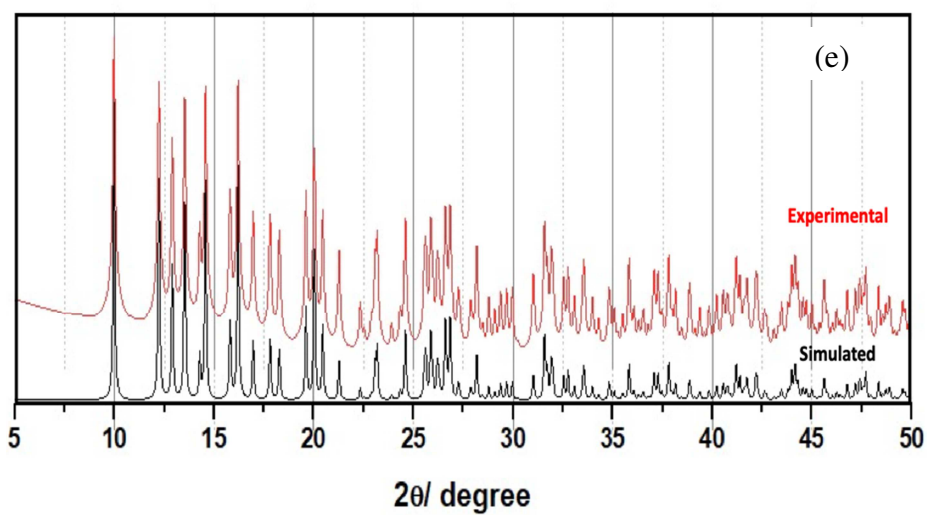
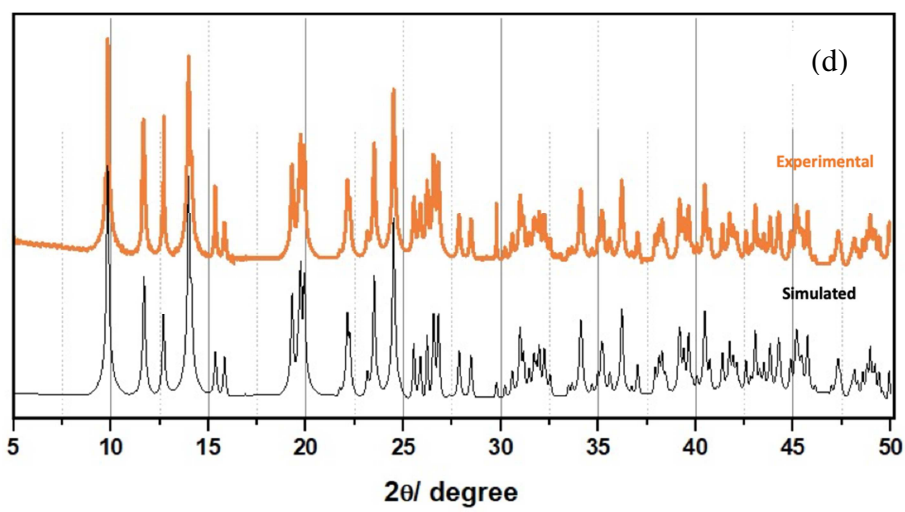
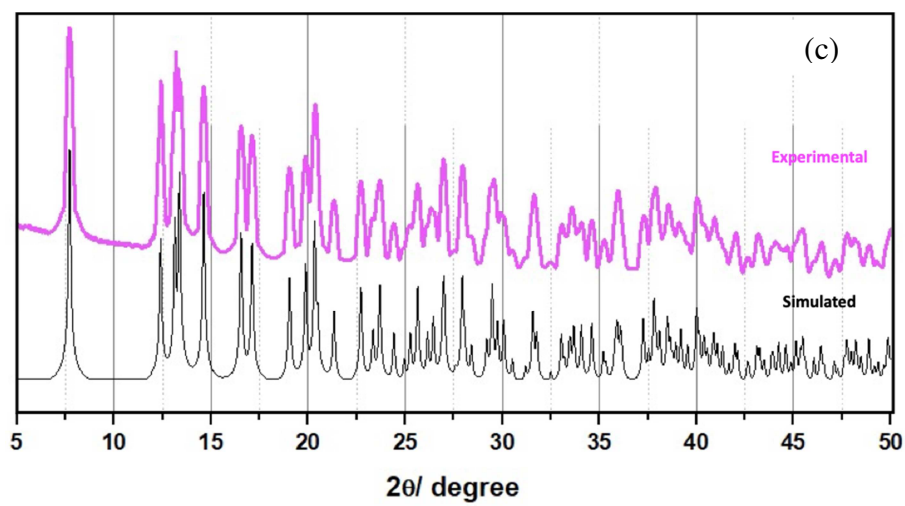
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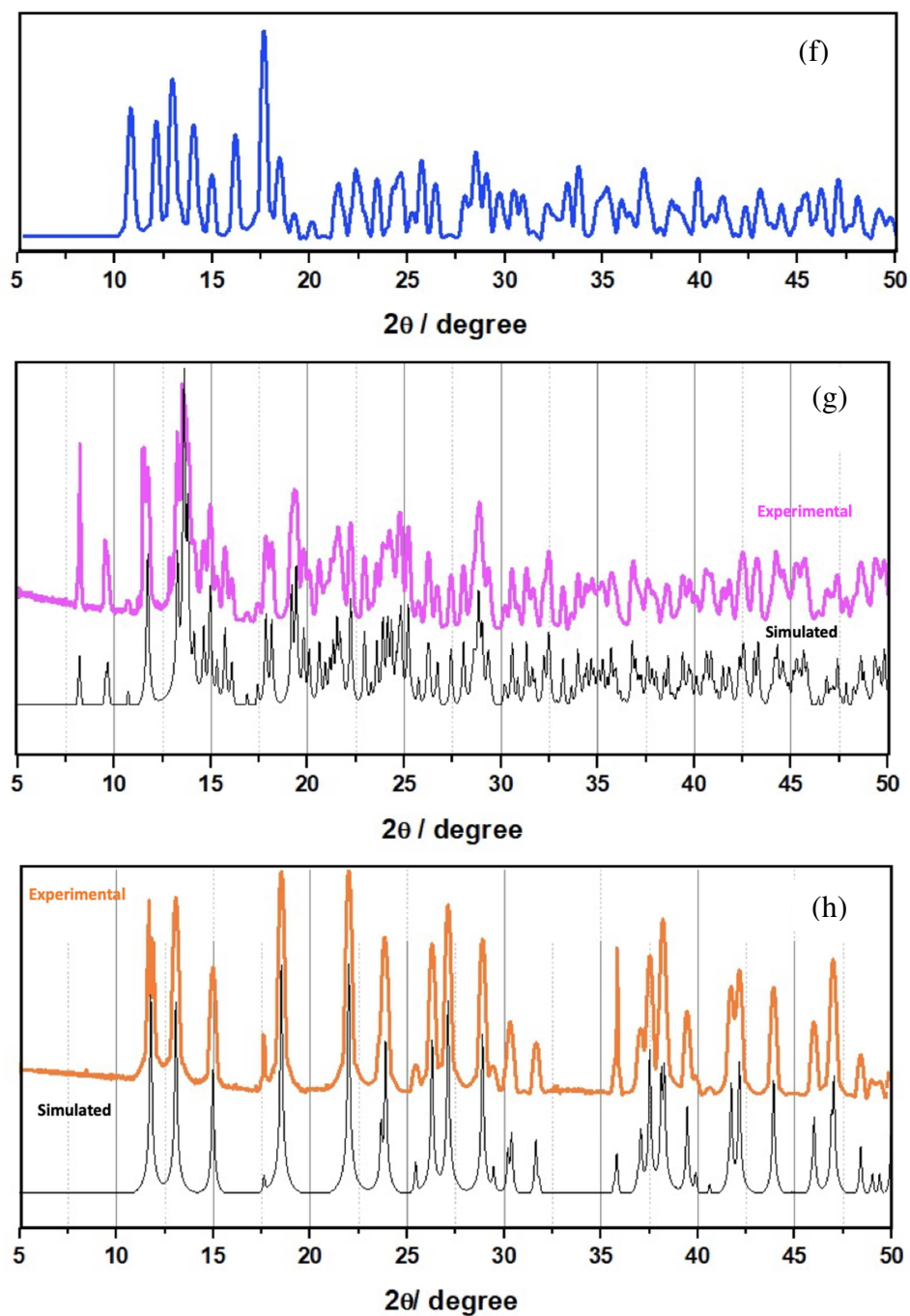


Figure S1. PXRD patterns for the title complexes (a) [Ni1]; (b) [Ni2]; (c) [Ni3]; (d) [Ni4]; (e) [Cu1]; (f) [Cu2]; (g) [Cu3]; (h) [Cu4]. The experimental patterns of each complex is matched with its corresponding simulated PXRD pattern from the crystal data. The experimental PXRD pattern of complex [Cu2]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

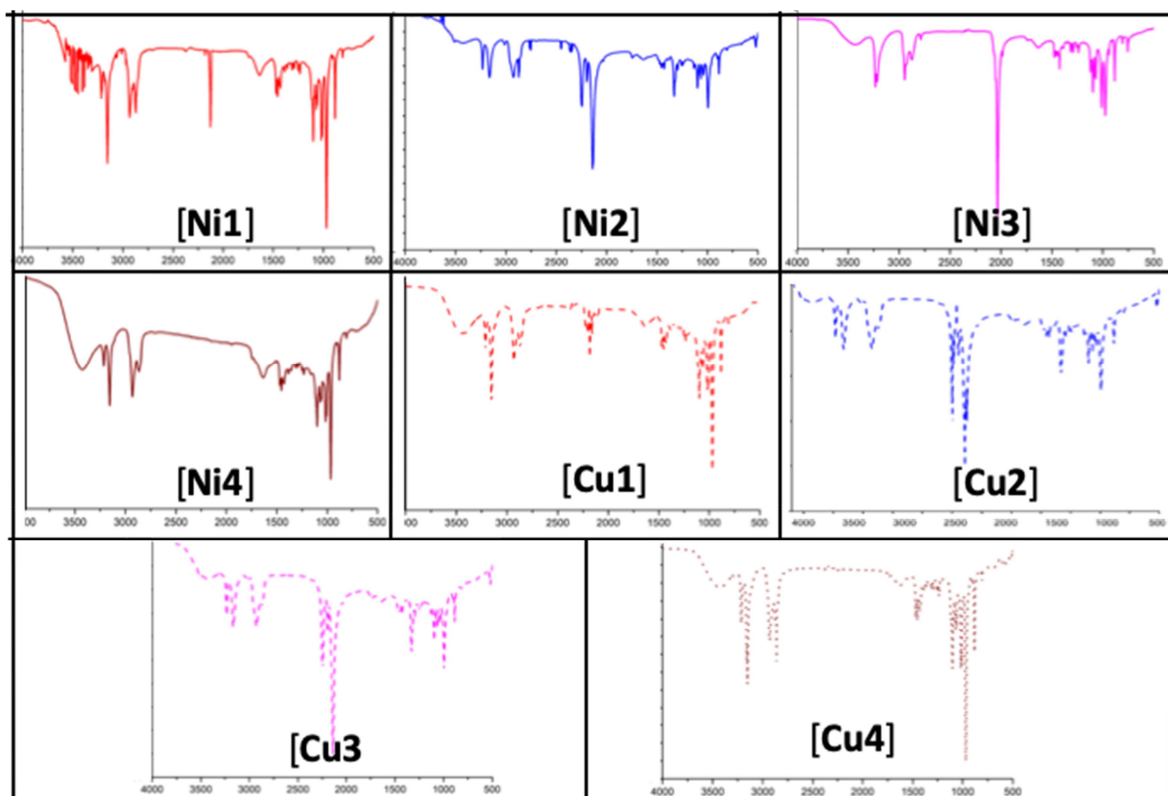


Figure S2. FTIR spectra for the title complexes.

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 ⁱⁱⁱ	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]**; ⁱ1/2-X, 1-Y, 1/2+Z; ⁱⁱX, 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]**; ⁱ1/3+Y-X, 2/3-X, -1/3+Z; ⁱⁱ1-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, 1/2-y, 1-z; ⁱⁱ2-x, 1/2+y, 1/2-z; ⁱⁱⁱ2-x, -1/2+y, 1/2-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 (°)	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 (°)
1.	 [Ni(cyclen) ₂][Pt(CN) ₄] ₂ ·6H ₂ O ^[S1]	2.07-2.14	7.462	39.300 38.291
2.	 [Ni(cyclen) ₂][Ni(CN) ₄] ₂ ·6H ₂ O ^[S1]	2.07-2.13	7.245	38.484 38.231
		2.02-2.11	8.610	36.217 35.829

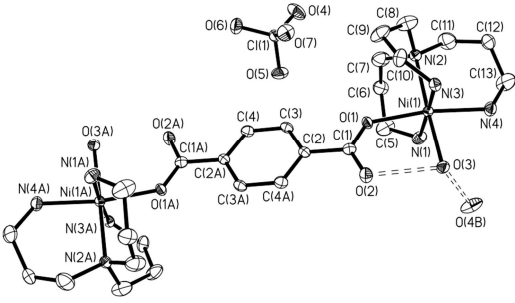
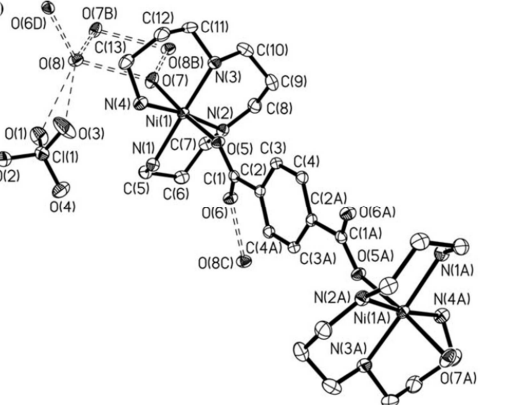
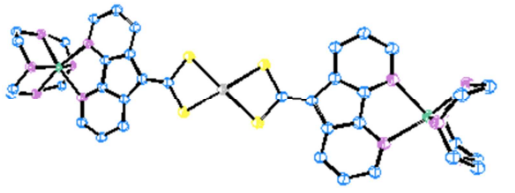
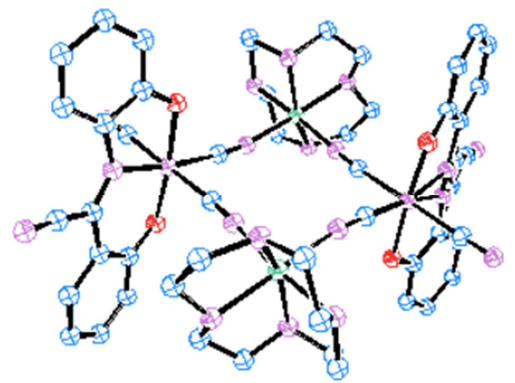
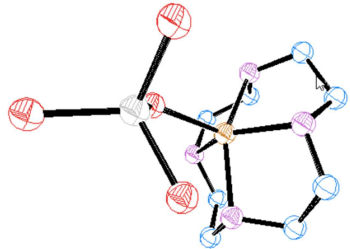
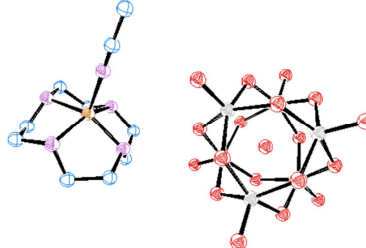
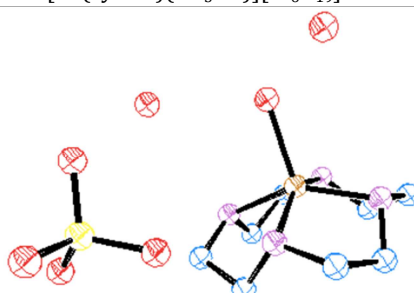
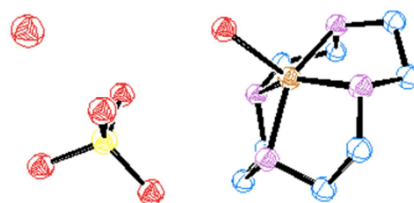
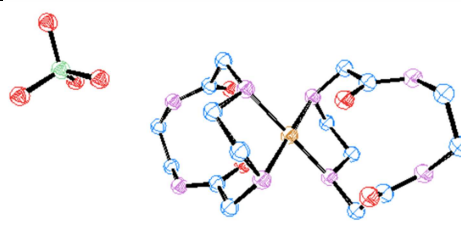
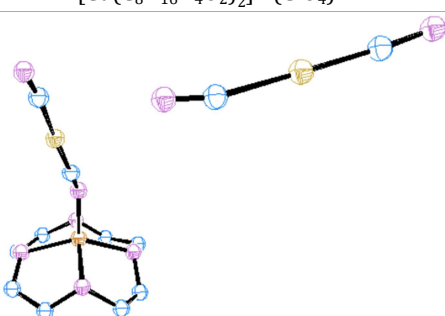
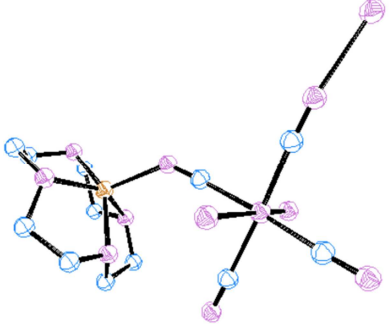
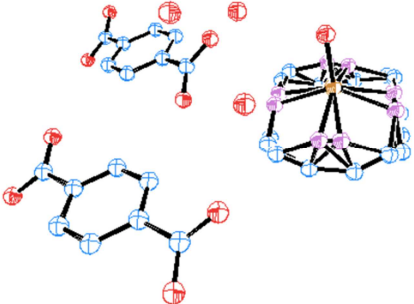
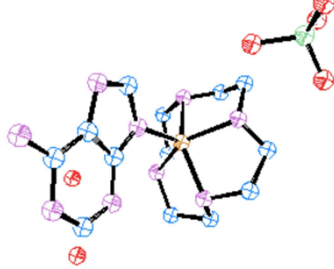
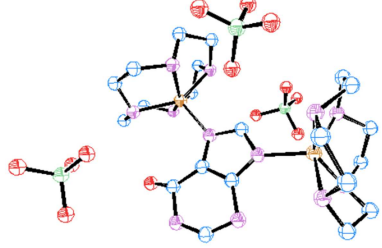
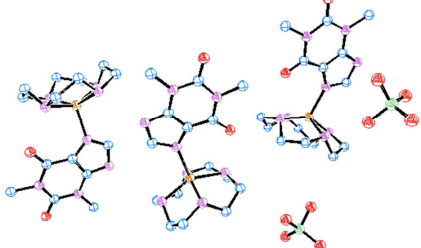
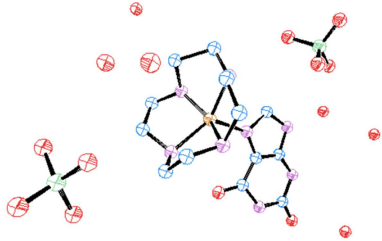
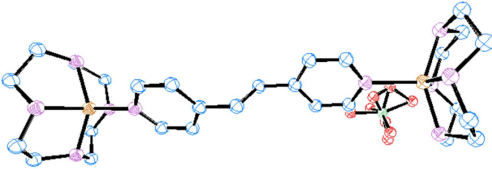
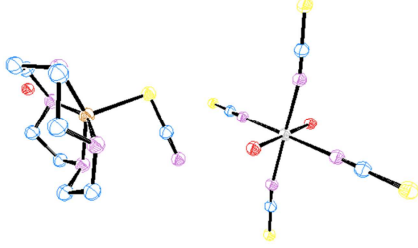
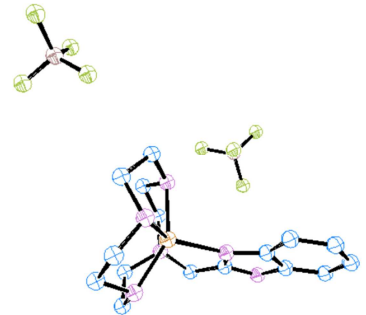
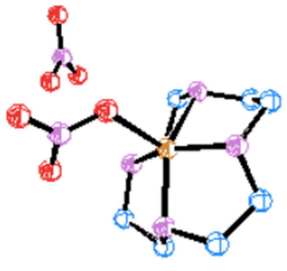
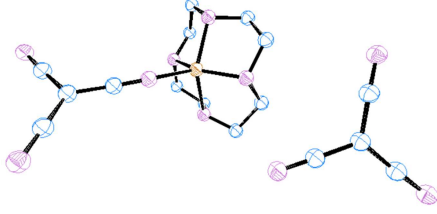
	$[\text{Ni}_2(\text{cyclen})_2(\text{tp})](\text{ClO}_4)_2$ [S2]	2.07-2.12	8.231	37.424
				
	$[\text{Ni}_2(\text{trpn})_2(\text{tp})(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ [S2]	2.09-2.14	9.113	36.223
				
	$[\text{Ni}_2(3,3,3\text{-tet})_2(\text{tp})(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ [S2]	2.09-2.11	10.313	38.318
				
	$[(\text{cyclenNi})_2\text{PdL}_2]^{2+}$ [S3]	2.10-2.13	7.664	39.359
				
	$[\text{Ru}^{\text{IV}}_4\text{Ni}^{\text{II}}_2(\mu^3\text{-Ome})_2(\mu\text{-Ome})_2(\mu\text{-N})_2(\mu\text{-N}_3)_2(\mu\text{-Ophenoxy})_2(\text{sap})_4(\text{MeOH})_4] \cdot 8\text{MeOH}$ [S3]			

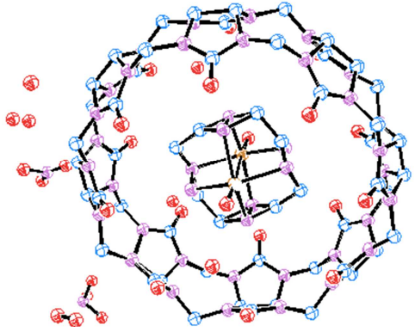
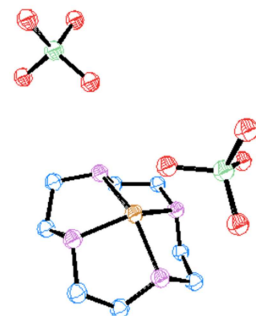
Table S4. Selected distances and dihedral angle of cyclen in reported Cu(II) complexes with cyclen.

S.No.	Complex	Cu-Ncy (Å)	Dihedral angle (°)
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1.	 <p>[(cyclen)CuMoO₄]₂(H₂O)₂ [S4]</p>	2.03-2.04	1.213
2.	 <p>[Cu(cyclen)(CH₃CN)][W₆O₁₉] [S5]</p>	2.00-2.04	0.929
3.	 <p>[Cu(cyclen)(H₂O)](SO)₄2(H₂O) [S6]</p>	2.02-2.03	0.245
4.	 <p>[Cu(cyclen)(H₂O)](SO)₄(H₂O) [S6]</p>	2.01-2.03	1.481
5.	 <p>[Cu(C₈H₁₆N₄O₂)₂].2(ClO₄) [S7]</p>	2.03-2.08	1.991
6.	 <p>[Cu(cyclen)(N(CN)₂)](N(CN)₂) [S7]</p>	1.90-2.04	2.809

7.	 <p>[Cu(cyclen)(CN)₂(N(CN)₄)]^[S7]</p>	1.98-2.03	2.422
8.	 <p>[Cu(Cyclen)H₂O](Tpa)·3H₂O^[S8] Tpa = Dianion of Terephthalic Acid</p>	2.00-2.07	2.597
9.	 <p>[Cu(cyclen)(adeninato)]·ClO₄·2H₂O^[S8]</p>	2.02-2.06	3.725
10.	 <p>[{Cu(cyclen)}₂(hypoxanthinato)]·(ClO₄)₃^[S8]</p>	2.00-2.04 2.01-2.08	0.006 0.150
11.	 <p>[Cu(cyclen)(theophyllinato)]₃·(ClO₄)₃·2H₂O^[S8]</p>	2.01-2.07 2.03-2.06	1.900 0.640

12.	 <p>[Cu(cyclen)(xanthinato)]·(0.7ClO₄)·(0.3ClO₄)·3H₂O·(0.5H₂O)₃[S⁸]</p>	2.01-2.07	3.625
13.	 <p>[Cu(cyclen)(4,4'-bipy)](ClO₄)₂[S⁹]</p>	2.02-2.03 2.02-2.04	0.305 0.548
14.	 <p>[Cu(SCN)(C₈H₂₀N₄)]₂·[Ca(NCS)₄(H₂O)₂]·2H₂O[S¹⁰]</p>	2.02-2.05	0.359
15.	 <p>CuL¹](BF₄)₂ [S¹¹] L¹=1-(benzimidazol-2-ylmethyl)-1,4,7,10-tetraazacyclododecane</p>	2.00-2.08	3.451
16.	 <p>[Cu(Cyclen)(NO₃)]NO₃[S¹²]</p>	2.00-2.03	1.723
17.	 <p>[Cu(C₄N₃)(C₈H₂₀N₄)](C₄N₃)[S¹³]</p>	2.01-2.30	0.023

18.	 <p>[Cu(Cyclen)(H₂O)]²⁺[CB_n]^[S14] CB= Cucurbit-[n] uril ; n = 5, 7, and 8</p>	2.06-2.07	0.274
19.	 <p>[Cu(cyclen)](ClO₄)₂ [S15]</p>	2.01-2.02	1.474

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