

The versatility of 1,4,8,11-tetraazacyclotetradecane (cyclam) in the formation of compounds of Co^{2+} , Ni^{2+} , Cu^{2+} , and Zn^{2+} with metal ions in and out of the cyclic ligand ring

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Abstract

Herein we report the results of preparing metal compounds (where the metal ions are Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+}) with the cyclic ligand 1,4,8,11-tetraazacyclotetradecane [cyclam] under a variety of conditions of metal-ligand ratios and solvent media. In all cases, we used metal $\text{Cl}_2 \cdot n\text{H}_2\text{O}$ salts (except for anhydrous CoCl_2), as specified. Outcome: we isolated species with a four-coordinate metal in the N4 cavity of the ligand alone, and also with either one or two additional axial ligands. Those axial ligands can be (a) a single chloride, leading to penta-coordinated⁺ products; (b) two chlorides, leading to octahedral-neutral compounds; (c) two waters, giving rise to hexa-coordinated [(cyclam)metal(H_2O)₂]²⁺ species. Finally, in the case of HCl added to the reaction medium, the cyclam can be di-protonated and appears as [(cyclam) H_2]²⁺ in the crystals. With such a variety of products, it is not surprising that since the metal coordination numbers vary, the cyclam ligand stereochemistries are thereby affected. Interestingly, the [(cyclam)metal] species are invariably hydrogen-bonded to one another in infinite strings of two kinds: (1) those for which the crystal's $Z' = 1$ have single strings; (2) when $Z' = 2$, there is a pair of homogeneous strings attached to one another by a variety of hydrogen-bonding linkages. Finally, we observed an interesting pair of hydroxonium cations: the first is hydroxonium cations in a pleated 2-D sheet consisting of fused pentagons located between sheets of [(cyclam)metal] moieties; the second one is an infinite string of composition (H_3O^+)-(H₂O)-(H₃O⁺)-(H₂O)-(H₃O⁺)-(H₂O)-(H₃O⁺)...

Keywords

1,4,8,11-Tetraazacyclotetradecanate ligand = (cyclam)
 Co^{+2} , Ni^{2+} , Cu^{2+} , Zn^{2+} complexes
 $[(\text{cyclam})\text{H}_2]^{2+}$ ions
 polychlorometallate anions
 unusual hydroxonium cations
 infinite 2-D sheets of multiply-charged hydroxonium cations

1. Introduction

Hereafter, (a) cyclam = 1,4,8,11-tetraazacyclotetradecane; (b) when useful, we will refer to data in the Cambridge Crystallographic Structural Database (CSD) [1] using a six letter acronym, such as **QADPAM** which will allow the reader direct access to the source when this information is needed.

The reactions described below produce two classes of products: (a) those with M^{2+} within the coordinating cavity of the cyclam ligand, thereby producing $[\text{cyclam M}]^{2+}$ cations (with $\text{M} = \text{Co}^{2+}$, Ni^{2+} , Cu^{2+} , Zn^{2+}); (b) those where the cyclam is 2+ charged by protonation and, is, thus, metal free. In the latter case, the charge compensating species is found to be a MCl_4^{2-} dianion.

We have prepared and determined the structures at 100K (or at 296 K) of the 2+ ions of the following species:

- (A) Trans-dichloro-Co(II)(1,4,8,11-tetraazacyclotetradecanate) $\cdot$ 1.9 CHCl_3 ,
 $[\text{C}_{10}\text{H}_{24}\text{Cl}_2\text{CoN}_4] \cdot 1.9 \text{CHCl}_3$; $\text{C}_{11.9}\text{H}_{25.9}\text{Cl}_{17.7}\text{CoN}_4$; CCDC# 2267413;
- (B) Bis-trans-dichloro-Ni(II)(1,4,8,11-tetraazacyclotetradecanate)(hydroxonium)-chloride
 hexahydrate $[\text{C}_{10}\text{H}_{24}\text{Cl}_2\text{N}_4\text{Ni}][(\text{H}_{15}\text{O}_7^+)(\text{Cl})]$; $\text{C}_{30}\text{H}_{102}\text{Cl}_{10}\text{N}_{12}\text{Ni}_3\text{O}_{14}$; CCDC# 1973426;
- (C) Catena-[Cu(II)(1,4,8,11-tetraazacyclotetradecanate)(tetrachloro-cuprate)], $[\text{C}_{10}\text{H}_{24}\text{CuN}_4]$
 $[\text{Cl}_4\text{Cu}]$; $[\text{C}_{10}\text{H}_{24}\text{Cl}_4\text{Cu}_2\text{N}_4]$; CCDC# 1973428;
- (D) (Trans-diaquo)[Zn(II)(1,4,8,11-tetraazacyclotetradecanate)]bis{[chloro-Zn(II)(1,4,8,11-tetraazacyclotetradecanate)](dichloride)dihydrate}, $[\text{C}_{10}\text{H}_{24}(\text{H}_2\text{O})_2\text{N}_4\text{Zn}]$
 $[\text{C}_{10}\text{H}_{24}\text{ClN}_4\text{Zn}]_2(2\text{Cl})_2(\text{H}_2\text{O})_2$; $\text{C}_{30}\text{H}_{80}\text{Cl}_6\text{N}_{12}\text{O}_4\text{Zn}_3$; CCDC# 1973429;
- (E) Bis-(1,4,8,11-tetraazacyclotetradecane)(dichloride)(tetrachloro-zincate),
 $[\text{C}_{10}\text{H}_{28}\text{N}_4](\text{Cl})_2(\text{Cl}_4\text{Zn})$; $[\text{C}_{10}\text{H}_{28}\text{Cl}_6\text{N}_4\text{Zn}]$; CCDC# 1973430.

2. Experimental

2.1 Syntheses and Crystallization

Synthetic Procedures for Compounds (A), (B), (C), (D), (E): (All chemicals were purchased either from Sigma-Aldrich, or from ThermoScientific, or from Strem Chemicals (anhydrous CoCl_2), and were used without further purification.)

N.B.: In all cases, crystals of optimal quality and size for the X-ray diffraction data collection were found in the material isolated after each of the procedures described below.

- (A) **Co(II)(cyclam) complex:** The product we obtained in aqueous solution, under conditions similar with those given for Ni(II), Cu(II) and Zn(II) (given below) contained, invariably, the Co(III)(cyclam) complex; thus, we resorted to the non-aqueous method (using Schlenk-ware) described here. Weighed out 0.334 g of macrocycle (1.67 mmol) and 0.220 g anhydrous CoCl_2 (1.69 mmol; 1:1 mole ratio) into two 25 mL oven-dried Schlenk flasks. Added 10 mL 200 proof EtOH to each flask. Both solutions were sparged with N_2 via needle for 5 minutes and then attached to a standard Schlenk line. The CoCl_2 suspension was added dropwise to the macrocycle solution via cannula transfer; immediately, the solution changed to brown and then over a period of 10 minutes became a pink-brown suspension. The reaction was stirred for 30 minutes. The suspension was concentrated to precipitate the maximum amount of pink product, and the brown supernatant was decanted via cannula into a frit and filtered to recover any leftover product. The pink powder of cobalt(II) cyclam complex (0.343 g, % yield) was then dried in vacuo and transferred into a N_2 -purged glovebox for further characterization. The air and water-sensitive solid was only soluble in DCM and CHCl_3 . Crystals suitable for XRD were grown from a concentrated solution of CHCl_3 slowly evaporating over time.
- (B) **Ni(II)(cyclam) complex:** Two solutions were prepared separately: (a) 1.0175g of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (4.28 mmol) were dissolved in 20 mL of MeOH; and (b) 0.84 g of cyclam (4.19 mmol; 1:1 mole ratio) in 10 mL of MeOH. Slowly adding (b) to (a) resulted in a brown solution that was treated with a dropwise addition of 2 mL of 12 M HCl – no color change resulted. That solution was then filtered through paper and heated to reduce the volume, and set aside to crystallize at RT. Green crystals resulted, one of which was used for diffraction experiments.
- (C) **Cu(II)(cyclam) complex:** Two solutions (a) and (b) were prepared: (a) contained 3.36g of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (19.71 mmol) in 10 mL of MeOH, while (b) contained 0.44g of cyclam (2.20 mmol; 9:1 mol ratio) in 10 mL of MeOH and 10 mL of THF. The latter was then heated to *ca.* 70 °C and dropwise addition of (a) into it resulted in a dark purple solution and a small amount of a brown solid, which were filtered through paper. The filtrate produced well-formed purple crystals suitable for additional X-ray studies.
- (D) **Zn(II)(cyclam) complex:** Again, solutions (a) and (b) were prepared, which contained: (a) 0.5463g of ZnCl_2 (4.01 mmol) were dissolved in 10 mL of water and (b) 0.4325g of cyclam (2.16 mmol; 1.8:1 mol ratio) in 10 mL of MeOH. Slow addition of (b) into (a) was followed by the dropwise addition of 1 mL of 12 M HCl, which produced a crop of white crystals upon standing.

(E) Zn(II)(cyclam) complex: Finally, solution (a) was obtained by stirring 2.8g of ZnCl_2 (20.54 mmol) in the minimal amount of MeOH at RT, while solution (b) was prepared by trying to dissolve 0.43g of cyclam (2.15 mmol; 9.6:1 mol ratio) in 10 mL of THF, with stirring. Failure of dissolution led to warming the cyclam solution to *ca.* 70 °C and the addition of 5 additional mL of MeOH. Then, (a) was slowly added to (b) and 10 mL of 12 M HCl were added to the (a,b) mixture and stirring continued for 1.5 hrs, resulting in a crop of white crystals, which were filtered and used to collect the X-ray data.

2.2 X-Ray Diffraction Data Collection and Processing

The SXRD data for complex (A) was collected at 100K on a Rigaku XtaLAB Synergy-S Dual Source diffractometer with a PhotonJet Cu-microfocus source ($\lambda = 1.54178 \text{ \AA}$) and a HyPix-6000HE hybrid photon counting (HPC) detector. To ensure completeness and desired redundancy, the data collection strategy was calculated using *CrysAlis* PRO [2]. Subsequent data processing was also performed in *CrysAlis* PRO. Using the SCALE3 ABSPACK scaling algorithm [3], empirical and numerical (Gaussian) absorption corrections were applied to the data (faces were determined using face-indexing in *CrysAlis* PRO). The structure was solved *via* intrinsic phasing methods, first in the Olex2 [4] graphical user interface and later in SHELXT [5] and refined by full-matrix least-squares techniques against F^2 (SHELXTL) [6]. The final structural refinement included anisotropic temperature factors on all non-hydrogen atoms. All H atoms were placed either according to their electron density Q-peaks or were attached via the riding model in idealized positions using suitable HFIX commands. Data processing, Lorentz-polarization, and face-indexed numerical absorption corrections were performed using SAINT, APEX, and SADABS computer programs [7-9]. It was found that some of the CHCl_3 of crystallization was lost during data collection, and its occupancy was refined to be 0.95. A crystal of each, (B) through (E), was mounted on a Bruker APEXII X-ray diffractometer using graphite-monochromated $\text{CuK}\alpha$ ($\lambda = 1.54178 \text{ \AA}$) radiation, oriented, and full spheres of data were collected. For (B), (D) and (E), the data were collected at 296K. The data for (C) were collected at 100K. Crystals of these compounds were secured to a micromount fiber loop using Paratone-N oil. Crystal dimensions as well as the pertinent crystal information for all five compounds are given in Table 4. Structures (B) – (E) were solved by direct methods and refined by full-matrix least-squares methods on F^2 , using the SHELXTLV6.14 program package [6]. All the H atoms were found in electron-density difference maps, and were subsequently put in as riding models at idealized positions using suitable HFIX commands for all the cyclam and hydroxonium ions and waters. All non-hydrogen atoms were refined with anisotropic displacement parameters. For the five structures presented, structural and refinement parameters can be found in Table 1 and ORTEP representations of the structures are in the Supplementary Information.

Table 1. X-Ray structural parameters for (A), (B), (C), (D), (E)

Experimental details	(A)	(B)	(C)	(D)	(E)
Crystal data					
Chemical formula	C ₁₀ H ₂₄ Cl ₂ CoN ₄ ·1.9CHCl ₃	C ₃₀ H ₁₀₂ Cl ₁₀ N ₁₂ Ni ₃ O ₁₄	C ₁₀ H ₂₄ Cl ₄ Cu ₂ N ₄	C ₃₀ H ₈₀ Cl ₆ N ₁₂ O ₄ Zn ₃	C ₁₀ H ₂₈ Cl ₆ N ₄ Zn
M_r	556.96	1385.86	469.21	1081.86	482.45
Crystal system, space group	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/c$	Monoclinic, $C2/c$	Monoclinic, $P2_1/c$	Triclinic, $P-1$
Temperature (K)	102(2)	296(2)	100(2)	296(2)	296(2)
a, b, c (Å)	6.5901(3), 11.9679(5), 15.0843(5)	9.6978(4), 19.3716(4), 16.5744(3)	15.3904(4), 8.3138(2), 15.0745(6)	8.2836(3), 23.8296(7), 12.4158(4)	7.3764(6), 8.0873(6), 17.0720(13)
α, β, γ (°)	90., 98.194(3), 90.	90., 106.070(1), 90.	90., 113.912(1), 90.	90., 91.695(2), 90.	84.182(2), 85.439(2), 77.716(2)
V (Å ³)	1177.54(8)	2992.0(1)	1763.27(9)	2449.74 (14)	988.23 (13)
Z	2	2	4	4	2
Radiation type	CuK α	CuK α	CuK α	CuK α	CuK α
μ (mm ⁻¹)	13.796	5.734	8.508	5.090	9.176
Crystal size (mm)	0.030 x 0.040 x 0.270	0.170 x 0.297 x 0.654	0.088 x 0.234 x 0.269	0.154 x 0.185 x 0.644	0.119 x 0.370 x 0.408
Data collection					
Diffractometer	Rigaku Synergy XtalLAB	Bruker ApexII	Bruker ApexII	Bruker ApexII	Bruker ApexII
Absorpt. corr.	Numerical	numerical	numerical	numerical	numerical
$T_{\min}, T_{\max}$	0.295, 1.000	0.083, 0.505	0.283, 0.696	0.182, 0.538	0.108, 0.510
No. of measured, independent, obs. [$I > 2\sigma(I)$] refls	9325, 1605, 1457	27920, 5349, 5184	7647, 1546, 1488	22818, 4267, 4038	9191, 3304, 3137
Rint	0.069	0.030	0.030	0.034	0.035
$(\sin \theta / \lambda)_{\max}$ (Å ⁻¹)	0.547	0.606	0.605	0.606	0.605
Refinement					

R[F > 2 σ (F)], wR(F), S	0.059, 0.155, 1.06	0.023, 0.069, 1.14	0.027, 0.069, 1.10	0.024, 0.059, 1.07	0.028, 0.077, 1.05
No. of reflections	1605	5349	1546	4267	3304
No. of params.	121	377	99	281	191
No. of restraints	2	21	2	10	0
H-atom treatment	Mixed	mixed	mixed	mixed	constr
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (eA ⁻³)	0.971, -0.475	0.337, -0.289	0.979, -0.630	0.330, -0.333	0.509, -0.304
CCDC number	2267413	1973426	1973428	1973429	1973430

3. Results and Discussion

(A) Cobalt(II) cyclam · 1.9 CHCl₃ complex: [C₁₀H₂₀Cl₂CoN₄ · 1.9 CHCl₃] (A)

There is no simple 1,4,8,11-tetraazacyclotetradecaneCo(II) in the current CSD collection [1]. There is one entry, AGAMIF, that is an extremely complex species: bis(μ_2 -2-chloro)-(1,4,8,11-tetraazacyclotetradecane)-octakis(3,5-dimethyl-pyrazolato)-cobalt(II)-di-uranium(IV) dichloromethane solvate, in which the axial chloride ligands bridge a pair of the complex uranium moieties [10]. Thus, our complex is a unique species, which stands alone in this study by being prepared from anhydrous Co(II)Cl₂ in an air-free medium from a non-aqueous solvent (chloroform), which it incorporates into the lattice, as described below.

There is a rich, 3-dimensional, hydrogen-bonding network in these crystals, resulting in the need of using figures along two directions in order to avoid excessive cluttering. Figure 1 is a projection down the bisector of the *a*- and *b*-axes, showing the cobalt cations linked into strings made up of hydrogen-bonded (close contacts) N-H $\cdots$ Cl, while Figure 2 is close to an *a*-projection showing the relationship of the CHCl₃ molecules to the complex.

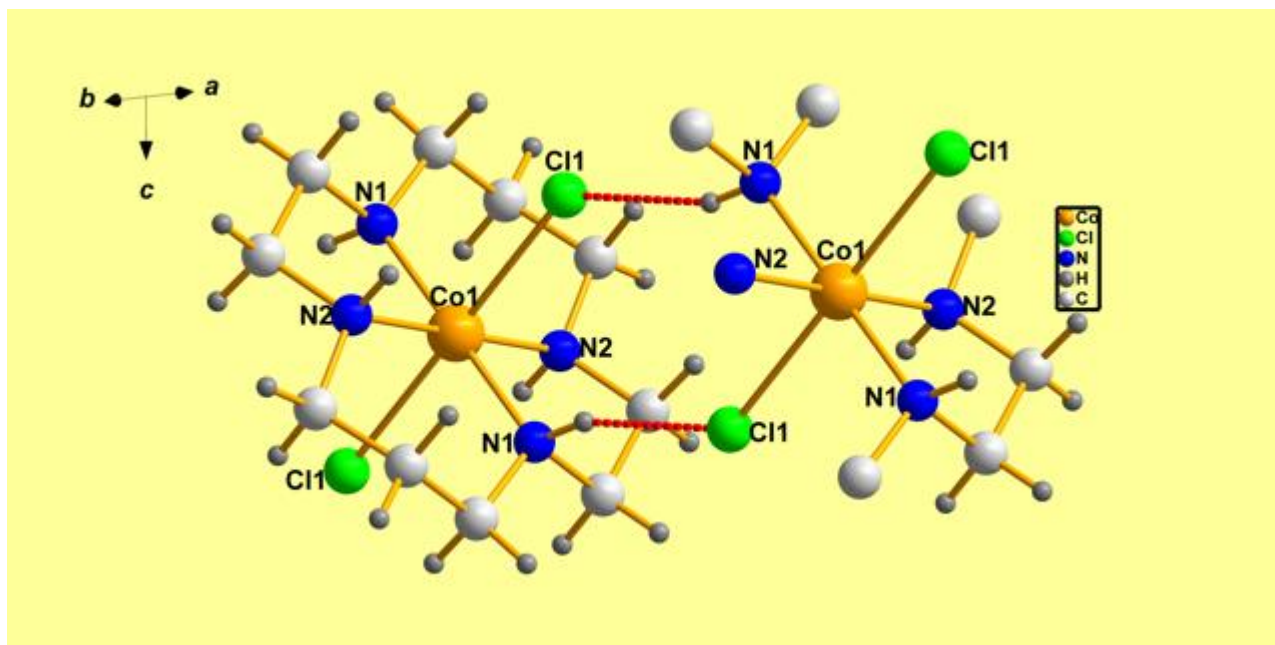


Figure 1. The molecular structure of Co(II) cyclam · 1.9 CHCl₃ complex showing the close contact between the H1 atom from N1 and Cl1 [$1-x, 1-y, 1-z$] = 2.410(18) Å. In order to avoid clutter, a portion of the ligand at right has been omitted;

There also are two other close contacts between the chloroform of crystallization and the H2 of N2, and from the H6 of the CHCl₃ and Cl1 of the cyclam (see Figure 2 below).

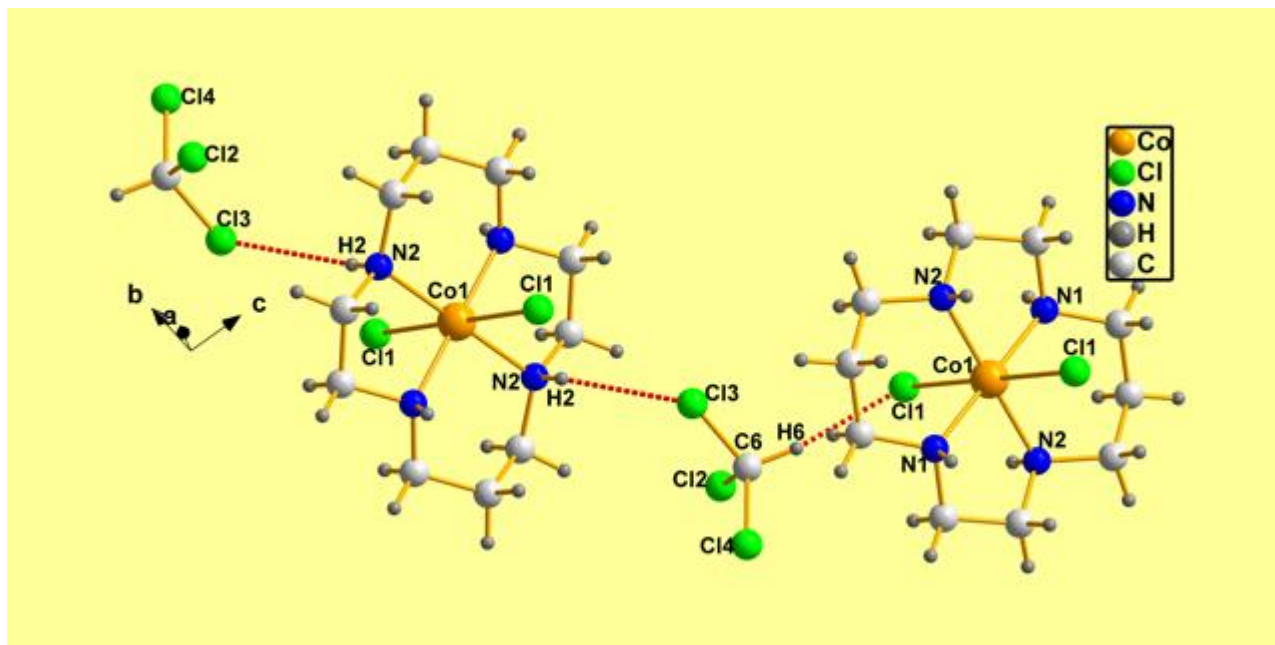


Figure 2. Infinite strings lie almost exactly on the *bc*-plane and extend along the bisector of *b* and $-c$. These two close contacts are between the H2 of N2 of the cyclam ring and the Cl3 of the chloroform of crystallization [$\text{H2}\cdots\text{Cl3} = 2.77(3) \text{ \AA}$], and from H6 of the CHCl_3 to $\text{Cl1}[0.5-x, 0.5+y, 0.5-z] = 2.373 \text{ \AA}$ of the cyclam. This latter close contact is much shorter than similar ones in the literature (2.567 and $2.599 \text{ \AA}$) [11].

(B) Nickel(II) (cyclam) complex:

Despite the fact that the Co(II) derivative was obtained from chloroform, while that for the remaining examples in this paper (**B**→**E**) were obtained from aqueous media, comparison of the packing of the $[(\text{cyclam})\text{M}]^{2+}$ cations ($\text{M} = \text{Co}$ and Ni) appearing in Figures 1 and 3 (just below), shows the common feature of being joined into strings by pairs of hydrogen bonds (close contacts) linking axial Cl to amino hydrogens of the adjacent molecules. The fact that such strings are essentially identical is quite remarkable given the marked difference in the content of their asymmetric units (more in the Discussion). And, again, because of the complexity of the asymmetric units, we must resort to multiple figures. Figure 3 depicts the hydrogen-bonded strings present in the Ni(II) specimen. Note the presence of Ni1 at a general position and a Ni2 at an inversion center $[0.50, 0.50, 0.50]$.

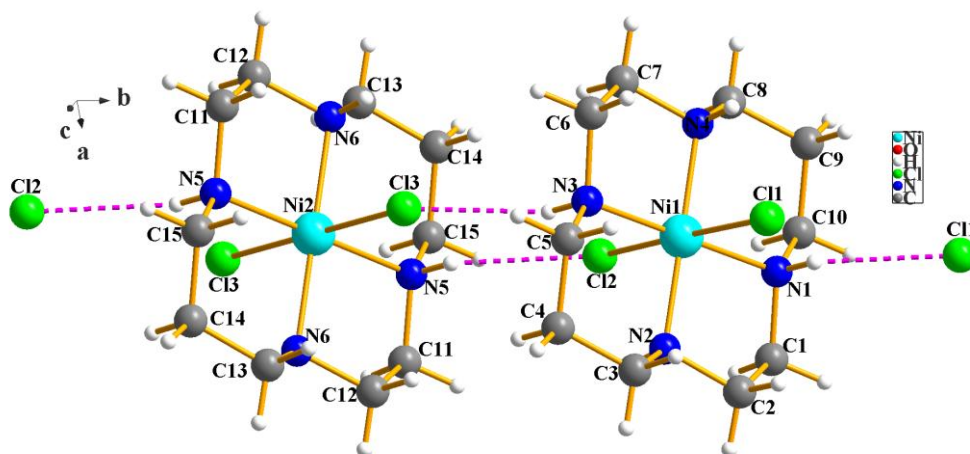


Figure 3. In **(B)**, Cl1 and Cl2 are H-bonded (close contacts) to the NH fragments of the metal ligand in infinite fashion, depicted by dotted lines. This arrangement, in pairs, is the same as that for the Co(II) complex shown in Figure 1. Note that, whereas chloroform molecules in **(A)** link the pairs of the string, **(B)** is homogenous throughout; *e.g.*, no intermediate linkage between pairs.

The *trans*-dichloro Cl1 and Cl2 anions are H-bonded to the NH fragments of the metal ligand. Despite the fact that the Co(II) has only one molecule in the asymmetric unit while Ni(II) has two (Ni1 at a general position and Ni2 at an inversion center), those strings share a common symmetry operation (2-fold screw along *b*, leading to the packing similarities observed (details follow in the Discussion).

Next, we depict in Figure 4 a larger fragment of the Ni(II) lattice, which is close to a *c*-projection. This view is useful for depicting the nature of the hydroxonium cation present in the lattice, as well as illustrating its role in linking the strings of the Ni(II)cyclam complexes together.

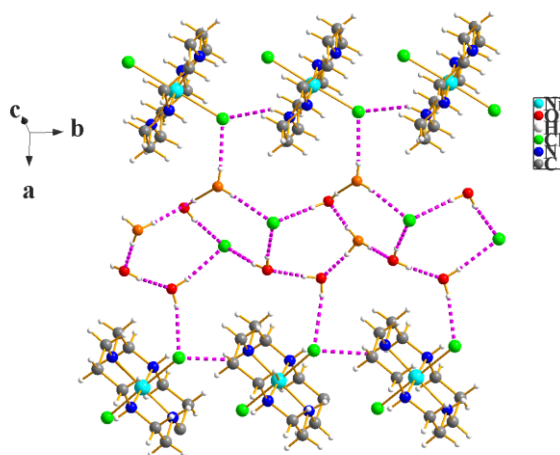


Figure 4. Interestingly, (H_3O^+), H_2O and Cl fragments form sheets between parallel rows of metal-amine ligand moieties; note that *bare* chloride anions play an important role in the formation of the hydroxonium cation, as depicted in both Figures 4 and 5 (below).

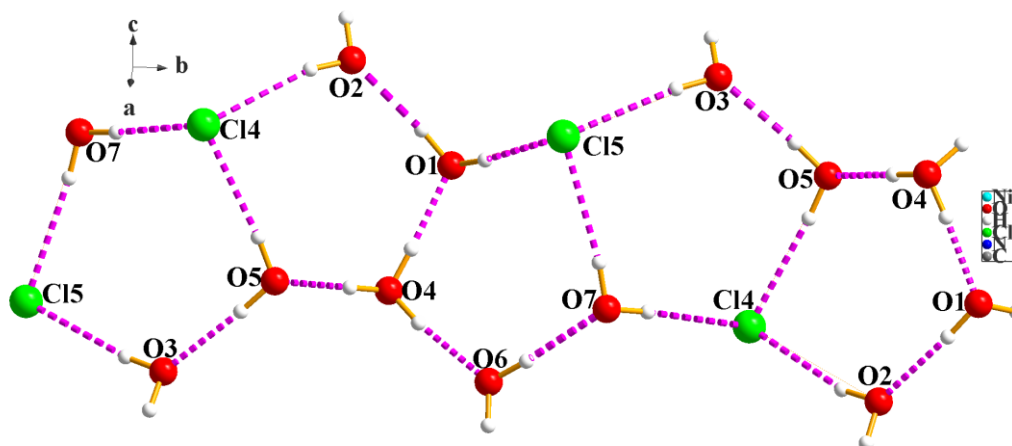


Figure 5. The H_3O^+ component is demarked by O4, which is surrounded by three linearly-bonded pairs of waters (denoted by O1-O2, O5-O3 and O6-O7) in an overall star arrangement never described before. See reviews [12-14].

Finally, another interesting and unexpected reason for the nature of the hydroxonium cation herein observed in the lattices of a coordination compound is due to a report by Kubitz [15], who stated that: “Properties and possible structures of hydronium trihydrate H_9O_4^+ and hexahydrate $\text{H}_{15}\text{O}_7^+$ are considered. From the 2330 minerals listed in Strunz’s mineralogical tables nineteen were selected that appear to contain $\text{H}^+ \cdot 4\text{H}_2\text{O}$ or $\text{H}^+ \cdot 7\text{H}_2\text{O}$, and the possibility of discrete H_9O_4^+ or $\text{H}_{15}\text{O}_7^+$ groupings existing in their crystal lattice is discussed. From a crystallochemical point of view the most probable examples of hydronium hydrate compounds are layer lattice minerals like H-montmorillonite, H-vermiculite, troegerite, H-meta-autunite, sabugalite, and hewettite.” We note as well that this is not the first time that solutions of coordinated compounds produce specimens of purely mineralogical interest, another example being the discovery that $\text{Na}_2[\text{Cu}(\text{CO}_3)_2] \cdot 3\text{H}_2\text{O}$, chalconitronite, was isolated from a solution of a copper coordination compound coordinated by [(3-aminopropyl)-di-(2-hydroxypropyl)]-amine [16].

This cation, $\text{H}_{15}\text{O}_7^+$, has also been described previously [17], see NEDBII in CCDC [1]. Unfortunately, that structure is partially disordered. A more closely related one [18] has been described before, which is an ordered species, as shown below in Figure 6.

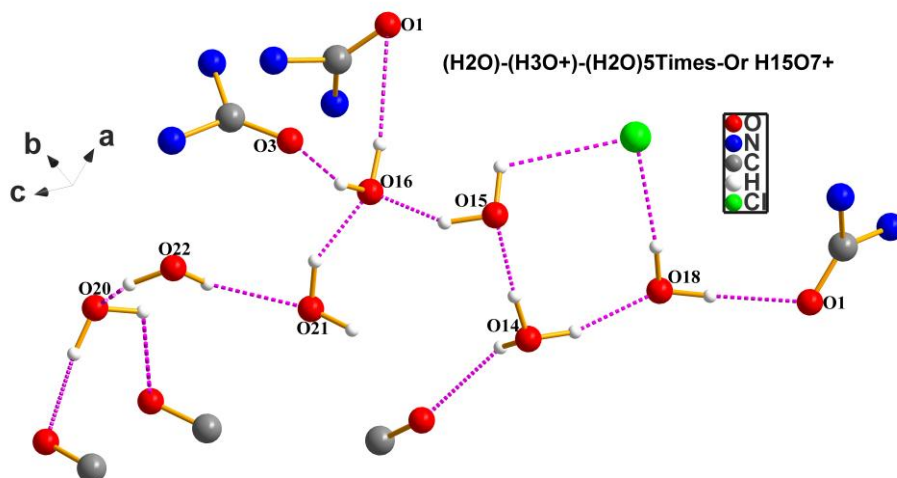


Figure 6. The stereochemistry of the cation $\text{H}_{15}\text{O}_7^+$ surrounded by the additional material in the lattice[18]. For additional information on the composition and stereochemistry of hydroxonium cations, see [12-14].

Because the nickel compound (**B**) contains two [cyclam-metal] species in the asymmetric unit, we generated an overlay diagram, Figure 7, depicting the remarkably similar diastereoisomeric relationship between them.

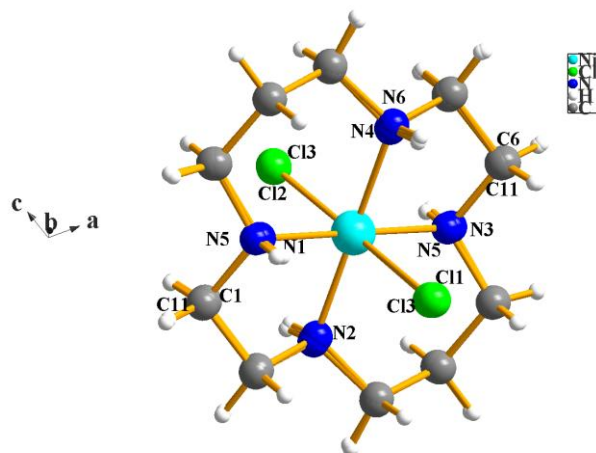


Figure 7. Overlay of Ni2 onto Ni1 using *Mercury* (from CCDC [1]). The resulting image was converted into this figure using *Diamond* [19]. Because of the near identity of the two species, it is impossible to place labels on both components, except in the few cases depicted above.

(C) Copper(II) cyclam complex:

The isolated product is a compound containing a CuCl_4^{2-} counter-anion and no axially-bonded chlorides on the coordinated copper cation, as depicted in Figure 8.

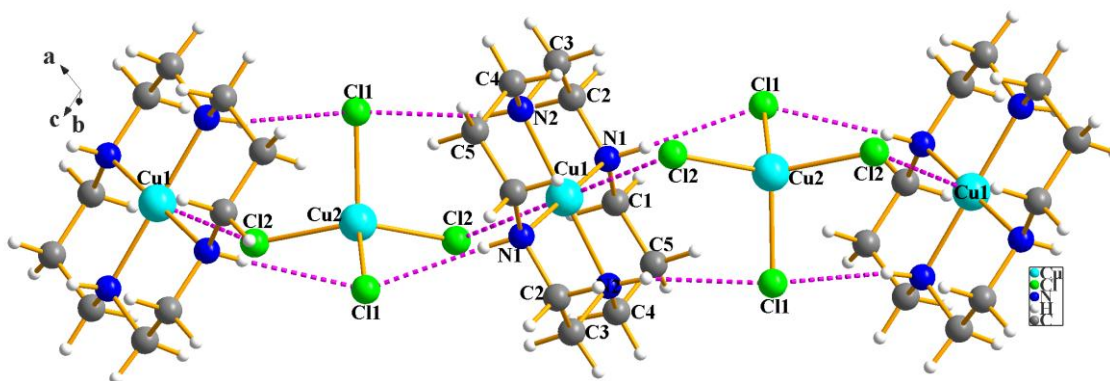


Figure 8. There are infinite hydrogen-bonded strings, approximately along the *a-c* vector direction, linked together by CuCl_4^{2-} anions that lie at inversion centers, as obvious from the atomic labels. That 3-D linkage is architecturally strong, being formed by six substantial close contacts (2.57-2.82 Å). Each of the two Cl1 of the CuCl_4^{2-} anion (by symmetry) form close contacts with the amine ligands; the other two (Cl2) form long [2.821 Å] axial bonds to the coordinated coppers (Cu1). Therefore, these are very tightly held strings with overall charge of zero.

We find it quite remarkable that this compound (**C**), constituted of neutral infinite chains, would be so well-behaved crystallographically, since the chains must be linked, at best, by residual asymmetric charges and/or van der Waal's forces. Therefore, we suggest that an attempt be made to prepare the entire series of Co(II), Ni(II), Cu(II) and Zn(II) of this composition, and observe the metal dependency of stereo- and physico-chemical properties of such group, especially if they turn out to be isomorphous and iso-structural.

(D) Zinc(II) cyclam complex:

With zinc, we obtained two different products from the pair of reactions detailed above. The first one, shown in Figure 9, contains a ligand-bound Zn(II) bearing a single axial chloride ligand, resulting in our only pentacoordinated metal compound of this series.

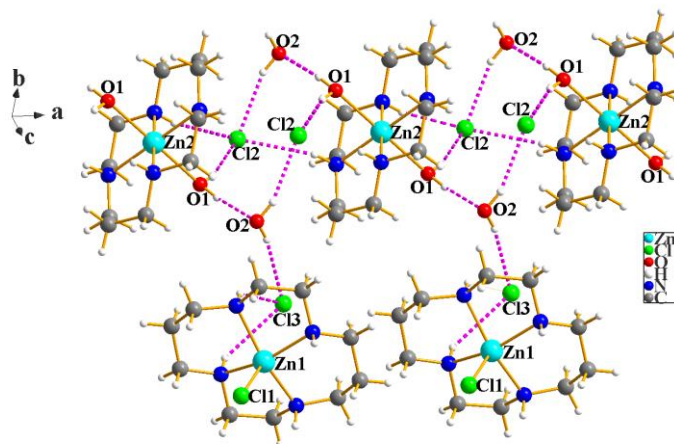


Figure 9. The approximate *c*-projection shows that Zn1 has a unique axial Cl1 bound as a counterion. This (Cl1) is not bound to anything else; Zn2 has two H₂O ligands (O1) in apical positions, depicted by red atoms here.

Each of the O1 ligand-bound waters is H-bonded to ionic Cl2 and also bonded to water O2, which is then hydrogen-bonded to water ligand O1 of Zn2. Finally, Cl3 is in close contact with H9 of O2 (2.353 Å), and to H2 of the amine $[x, 1/2-y, -1/2+z]$ (2.571 Å).

Once more, note that there is a common packing feature exhibited by the compounds described herein: namely that, irrespective of the metal and the overall composition, they form homogeneous or heterogeneous strings, which are then joined by hydrogen bonding adhesive material that glues the overall ensemble into tightly-packed 3-D arrays.

Interestingly CCDC [1] contains only two entries, AZCDHG [20] and POCXIO [21], for a metal having the central metal ligated by an unsubstituted cyclam and bearing a single axial chloride ligand, thus rendering the metal penta-coordinated. The former is a mercury complex with tetrachloromercurate(II) as anion and its structure is heavily disordered. Of additional interest is that the latter is also a Zn(II) derivative bearing a ZnCl_4^{2-} charge-compensating dianion in which one of its chlorines is 3.41 Å away from the coordinated zinc. Therefore, [21] and our structure (**D**) are unique, as far as we can find in our 2022 release of CCDC [1].

(E): Zinc(II) cyclam complex:

Species (**E**) is a compound bearing two chloride anions (Cl5 and Cl6), a Zn(II) in the anionic form of ZnCl_4^{2-} at a general position, and two independent tetra-protonated ligands at inversion centers, thus achieving charge balance. The R factor for this structure is 2.8%, which accounts for the precision with which the hydrogens were located, without which such a complex lattice would be difficult to assemble or to describe. The packing of the overall structure is quite complex - see Figure 10.

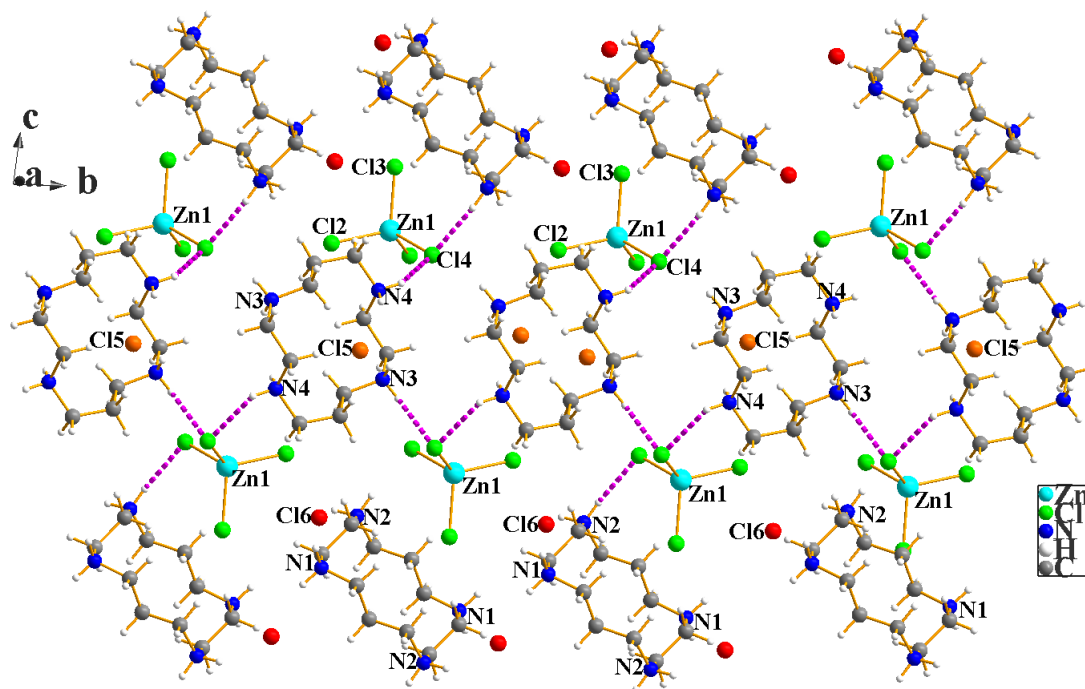


Figure 10. It is very difficult to display all of the elements of this crystal in a single diagram and, at the same time, achieve clarity. The line of sight chosen for this view shows all the elements present in the asymmetric unit in a single figure while avoiding cluttering overlap.

The function of the ZnCl_4^{2-} is to hydrogen bond one ring (characterized by N1, N2) to a second ring (characterized by N3, N4), as illustrated by the diagonal string of dotted purple lines. The hydrogen bonds of the ionic chlorides (Cl5 and Cl6, red and orange in the figure) have been eliminated because the clutter would be unacceptable in this “best” projection. Their function is as follows: Cl5 (orange) makes close contact, exclusively, with ring 1 (N3, N4) cations by linkages of length 2.193 and 2.262 Å. Cl6 (red) links exclusively ring 2 cations (N1, N2) by three close contacts of lengths 2.262, 2.311 and 2.422 Å.

Since it is obvious from Figures 9 and 10 that the conformation of the two cyclam cations is widely different, an overlap diagram was created similar to the process described above to generate Figure 7.

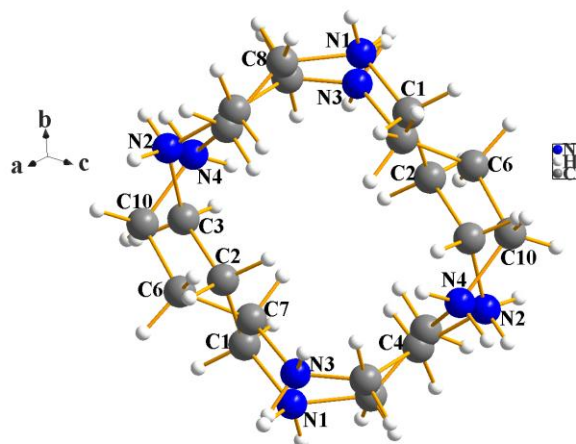


Figure 11. Overlay of the cations for species **(E)**, generated as described earlier using both *Mercury* [1] and *Diamond* [19]. Compare this with Figure 7 where the overlay is nearly perfect. In this case, the overlap is poor because of the major differences in torsional angles, likely to be the result of packing forces and hydrogen bonds and close contacts.

For all structures containing M^{2+} ions within the cyclam ring: the least-squares of the cyclam ring itself range between $-0.287(2)$ and $0.384(3)$ Å; for the cyclam rings in structure **(E)** only, the least-squares planes range between $-0.621(2)$ and $0.621(2)$ Å. All of the values of the least-squares planes are shown in Table T1 in the Supplementary Information.

The torsional angles N-C-C-N in complexes **(A)** $\rightarrow$ **(D)**, above, range between $51.9(4)$ and $68.4(7)^\circ$, with an average value of 55.2° , except for **(E)**, the complex where the metal is not coordinated by the cyclam. There, the torsional angles are $169.02(17)$ and $73.1(2)^\circ$ for the two different cyclams ($Z' = 2$); this very large difference in torsional angles is quite extraordinary and seems unlikely to be a charge phenomenon, since the Zn^{2+} and two H^+ cations provide the same positive charge to the (cyclam) ligand. Therefore, this is an interesting issue to be explored further, for which we offer only an experimental fact.

Upon examination of the torsional angles N-C-C-C and C-C-C-N in the larger ring of the cyclams, we note that in complexes **(A)** $\rightarrow$ **(D)**, these values range from $66.21(14)$ to $77.5(2)^\circ$, with an average value of 65.7° . For structure **(E)**, these torsional angles range from $60.1(3)$ to $175.05(18)^\circ$. Once more, these are experimental observations that merit further documentation and understanding. For the reader(s)'s convenience, a full list of these torsional angles is available in the Supplementary Information as Table T2.

Also, for completeness, the ORTEP diagrams of all five structures **(A)**, **(B)**, **(C)**, **(D)**, and **(E)** are shown as Figures S1, S2, S3, S4, and S5 in the SI.

4. Conclusions

The following conclusions are justified by the observations derived from the experimental results described above:

1. The cavity of the 14ane macrocycle (cyclam) can accommodate 2+ charged 3d-transition metal ions such as Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+} in three ways:

(a) insertion of the di-cation creates a simple planar species, as in **(C)**. In that case, a variety of compounds can be isolated depending on the charge compensating anion(s). Interestingly, in the 3d-series of metals there is no example recorded in CCDC [1] thus far where the counter-anions are simple halides. With any counter-anion and $R \leq 5.0\%$, there are only 14 examples, ten of which were from partial data sets collected at room temperature, thereby limiting the precision with which hydrogen-bonding networks could be defined.

(b) for those with one ligand in the fifth (axial) position, as in the case of **(D)**: there is a wide choice of possibilities, **(D)** itself being one, where the 5th ligand is a simple halide. There are none in CSD [1], if $R \leq 5.0\%$, irrespective of 3d metal. A *caveat* though, is that the structure **(D)** contains a second cation, bearing a pair of axial waters, which always is a possibility, either by itself or combined, as was the case here.

(c) finally, the metal(s) can bear two ligands in the axial positions and be six-coordinated. Here, the possibilities are very large, and some of our structures provide examples in which pairs of axial species are bonded to the metal. *Nota bene*: in the case of **(C)**, the copper cations are planar, four-bonded moieties, which, in the solid state, have a pair of symmetrical long Cu-Cl2 contacts of length 2.821 Å (see Figure 8, and its caption). An interesting possibility, not found here so far, is a substance bearing an anion (as Cl⁻) and a water molecule in the axial positions.

Thus, it seems that, if no other observations are made, the comments above provide ample reasons for additional investigations of the composition and stereochemistry of these complexes.

2. Again, on the basis of the above information, it seems fair to say that:

(a) if one wants to isolate the simple salts $\{[(\text{ane})\text{M}^{2+}]\text{X}_2\}$ (with $\text{M} = \text{Co}^{+2}$, Ni^{+2} , Cu^{+2} and Zn^{+2} , and $\text{X} = \text{Cl}$, for example) (except for the Co^{2+} complex, which has to be prepared in anhydrous conditions), the most promising recipe is to use MCl_2 as the starting material and add the ligand in a 1:1 ratio, and to add excess chloride via either NH_4Cl or KCl , because using HCl may result in the formation of hydroxonium cations such as in **(B)**. Those cations may well constitute attractive traps for hydroxonium cations of, currently, unknown compositions. Alternatively, one could obtain equally interesting ones of known composition but that are geometrical isomers of known ones (for examples of such occurrences, see [8-10]).

(b) by a careful addition of excess chloride, one could, in theory, obtain species with one or two chlorides in the axial positions; hence, the possibilities are extensive and will probably be difficult to guess at this stage what one may obtain out of such solutions, especially that one could obtain mixtures present in different ratios and solubility. If such be the case, careful microscopy of isolated crystalline

material will be called for. Finally, as for the mother liquor, it may be necessary to resort to chromatographic methods.

c) by judiciously changing the ratio of metal to [cyclam] ligand, one can obtain compounds in which the counter-anions are MCl_4^{2-} species, as in the case of (C) and (E). Given the ability of the MCl_4^{2-} to act as a strong hydrogen-bonding linkage to the [cyclam] metal^{2+} moieties, as in (C) and (E) (see Figures 8 and 10), this may be a possible way of generating some very interesting, and intricate, hydrogen-bonded networks. Finally, one could easily modify the nature of these [cyclam] metal^{2+} species by changing the size of the N_4 cavity given that the position of the metal would be affected.

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Author Contributions

Mah Noor is the undergraduate student who prepared most of the complexes under direct supervision of RAL. Hamza Chah and David Tresp are the undergraduate and graduate students, respectively, who prepared the Co(II)cyclam complex under anhydrous conditions using Schlenk-line techniques. IB and RAL wrote the manuscript.

Funding Source

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Competing Interests

The authors have declared that no competing interests exist.

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SUPPLEMENTARY INFORMATION:

Table T1. Least-Squares Planes for Structures (A), (B), (C), (D), and (E)

Structure	Atoms in plane	RMS of plane, (Å)	RANGE, (Å)
(A) Co(II) cyclam	C1 → C5, N1, N2	0.2515	-0.310(5) to 0.278(6)
	+ symmetry-related ones		
	Same, with Co inserted	0.3285	-0.297(5) to 0.274(6)
(B) Ni(II) cyclam	C1 → C10, N1 → N4	0.2503	-0.287(2) to 0.289(1)
	Same, with Ni inserted	0.2410	-0.288(3) to 0.289(3)
	C11 → C15, N5, N6	0.2432	-0.288(3) to 0.289(3)
	+ symmetry-related ones		
	Same, with Ni inserted	0.2337	-0.308(2) to 0.308(1)
(C) Cu(II) cyclam	C1 → C5, N1, N2	0.2583	-0.295(2) to 0.295(2)
	+ symmetry-related ones		
	Same, with Cu inserted	0.2496	-0.295(2) to 0.295(2)
(D) Zn(II) cyclam	C1 → C10, N1 → N4	0.2623	-0.287(2) to 0.367(1)
	Same, with Zn inserted	0.2792	-0.318(2) to 0.336(1)
	C11 → C15, N5, N6	0.2589	-0.305(1) to 0.305(1)
	+ symmetry-related ones		
	Same, with Zn inserted	0.2501	-0.305(1) to 0.305(1)
(E) $\text{ZnCl}_4^{2-} + \text{cyclamH}_2^{+2}$	C1 → C5, N1, N2	0.4471	-0.621(2) to 0.621(2)
	+ symmetry-related ones		

	C6 → C10, N3, N4	0.4392	-0.612(2) to 0.612(2)
	+ symmetry-related ones		

Table T2. Torsional Angles (°) for metal(cyclam) complexes (A), (B), (C), (D), and (E)

(A) Co(cyclam)	ATOMS IN RING	TORSIONAL ANGLE (°)
	N1-C1-C2-C3	68.4(7)
	C1-C2-C3-N2	-69.3(7)
	C2-C3-N2-C4	-177.2(5)
	C3-N2-C4-C5A	132.4(6)
	N2-C4-C5A-N1A	53.9(5)
	C4-C5A-N1A-C1A	107.0(4)
	C5A-N1A-C1A-C2A	-179.9(5)
	A = SYMM(1-x,1-y,1-z)	
(B) Ni(cyclam)	ATOMS IN RING	
	N1-C1-C2-N2	-53.73(13)
	C1-C2-N2-C3	172.7(1)
	C2-N2-C3-C4	179.7(1)
	N2-C3-C4-C5	66.21(14)
	C3-C4-C5-N3	-67.16(14)
	C4-C5-N3-C6	-176.1(1)
	C5-N3-C6-C7	-172.3(1)
	N3-C6-C7-N4	54.21(13)
	C6-C7-N4-C8	-174.4(1)
	C7-N4-C8-C9	-179.2(1)
	N4-C8-C9-C10	-67.27(14)
	C8-C9-C10-N1	66.70(14)
	C9-C10-N1-C1	178.3(1)
	C10-N1-C1-C2	173.5(1)
(B) Ni(cyclam)	ATOMS IN RING	
	N5-C11-C12-N6	-56.15(13)
	C11-C12-N6-C13	170.6(1)
	C12-N6-C13-C14	-178.0(1)
	N6-C13-C14-C15A	70.01(15)
	C13-C14-C15A-N5A	-69.42(14)
	C14-C15A-N5A-C11A	-179.5(1)
	C15A-N5A-C11A-C12A	-170.5(1)

	A = SYMM(1-x,1-y,1-z)	
(C) Cu(cyclam)	ATOMS IN RING	
	N1-C2-C3-N2	55.8(2)
	C2-C3-N2-C4	-171.37(18)
	C3-N2-C4-C5	179.67(18)
	N2-C4-C5-C1A	-70.4(2)
	C4-C5-C1A-N1A	70.1(2)
	C5-C1A-N1A-C2A	178.42(19)
	C1A-N1A-C2A-C3A	170.83(16)
	A = SYMM(0.5-x,0.5-y,1-z)	
(D) Zn(cyclam)	ATOMS IN RING	
	N1-C1-C2-N2	56.5(2)
	C1-C2-N2-C3	-164.60(16)
	C2-N2-C3-C4	172.51(16)
	N2-C3-C4-C5	-75.25(2)
	C3-C4-C5-N3	77.5(2)
	C4-C5-N3-C6	-175.79(16)
	C5-N3-C6-C7	163.16(16)
	N3-C6-C7-N4	-55.3(2)
	C6-C7-N4-C8	171.19(17)
	C7-N4-C8-C9	174.49(17)
	N4-C8-C9-C10	68.6(2)
	C8-C9-C10-N1	-67.3(2)
	C9-C10-N1-C1	-175.99(17)
	C10-N1-C1-C2	-172.83(16)
Zn(cyclam) · 2H₂O	ATOMS IN RING	
	N5-C12-C13-C14	70.7(3)
	C12-C13-C14-N6	-73.4(3)
	C13-C14-N6-C15	179.64(19)
	C14-N6-C15-C11A	-167.57(17)
	N6-C15-C11A-N5A	57.8(2)
	C15-C11A-N5A-C12A	-168.65(18)
	C11A-N5A-C12A-C13A	176.10(18)
	A = SYMM(1-x,1-y,-z)	
(E) (cyclam) ZnCl₄²⁻	ATOMS IN RING	
	N1-C1-C2-C3	173.54(19)
	C1-C2-C3-N2	-173.55(19)
	C2-C3-N2-C4	57.0(2)
	C3-N2-C4-C5	67.6(2)
	N2-C4-C5-N1A	-169.02(17)
	C4-C5-N1A-C1A	60.3(2)

	C5-N1A-C1A-C1A	58.6(3)
	A = SYMM(1-x,1-y,2-z)	
(cyclam) ZnCl ₄ ²⁻	N3-C8-C9-N4	-73.1(2)
	C8-C9-N4-C10	175.05(18)
	C9-N4-C10-C6A	-54.1(3)
	C7-C6-C10A-N4A	60.1(3)
	N3-C7-C6-C10A	-167.65(19)
	C6-C7-N3-C8	173.12(19)
	C7-N3-C8-C9	-62.08(2)
	A = SYMM(-x,2-y,1-z)	

Additional Materials

Figure S1: ORTEP for $[\text{C}_{10}\text{H}_{24}\text{Cl}_2\text{CoN}_4] \cdot \text{CHCl}_3$, (A): Ellipsoids are drawn at 40% probability level.

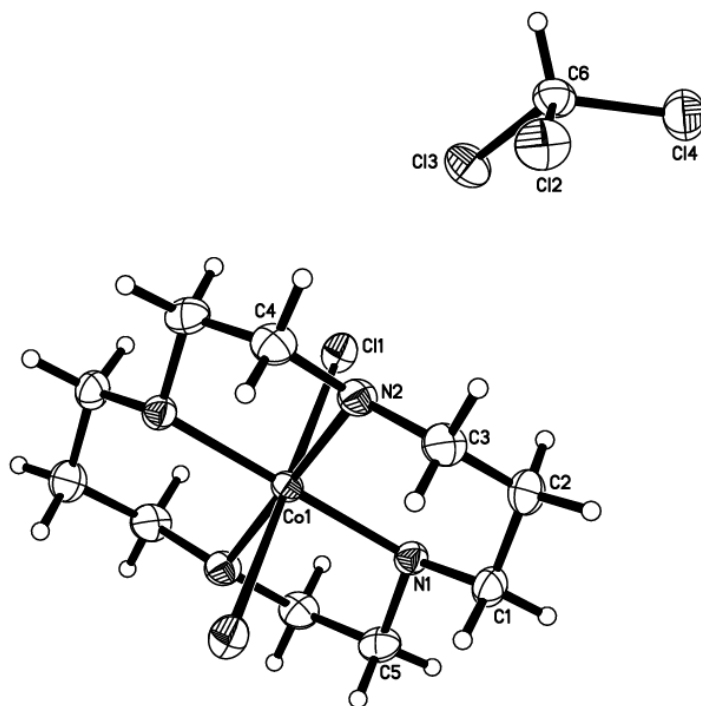


Figure S2: ORTEP for $[\text{C}_{10}\text{H}_{24}\text{Cl}_2\text{N}_4\text{Ni}][(\text{H}_{15}\text{O}_7^+)(\text{Cl}^-)]$, **(B)**: Ellipsoids are drawn at 40% probability level.

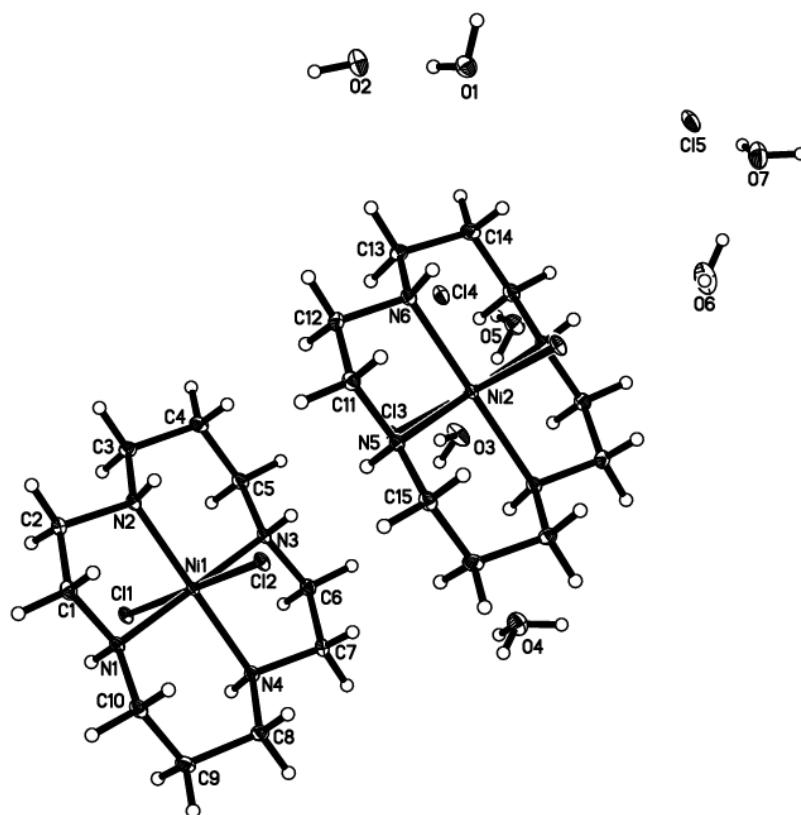


Figure S3: ORTEP for [C₁₀H₂₄CuN₄] [Cl₄Cu]; [C₁₀H₂₄Cl₄Cu₂N₄], (C): Ellipsoids are drawn at 40% probability level.

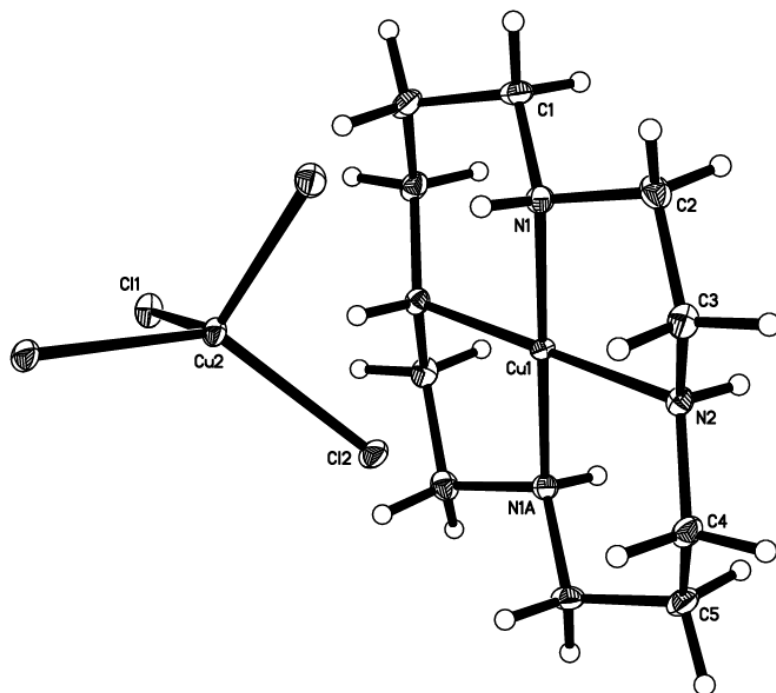


Figure S4: ORTEP for $[\text{C}_{10}\text{H}_{24}(\text{H}_2\text{O})_2\text{N}_4\text{Zn}][\text{C}_{10}\text{H}_{24}\text{ClN}_4\text{Zn}]_2(2\text{Cl})_2(\text{H}_2\text{O})_2$, (**D**): Ellipsoids are drawn at 40% probability level.

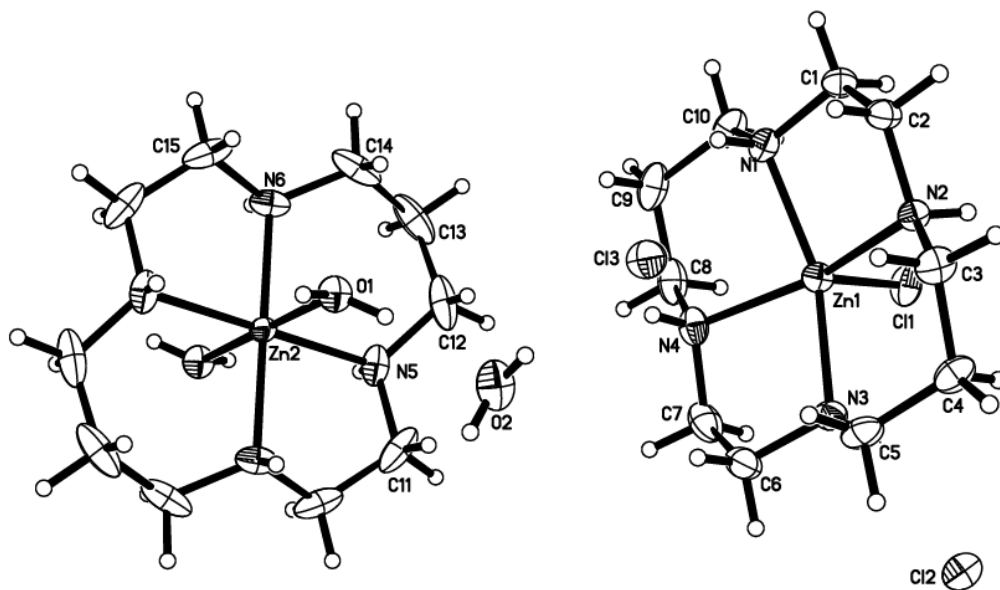


Figure S5: ORTEP for $[\text{C}_{10}\text{H}_{28}\text{N}_4](\text{Cl})_2(\text{Cl}_4\text{Zn})$, (**E**): Ellipsoids are drawn at 40% probability level.

