Electronic Supplementary Material (ESI) for ChemComm.

Covalent attachment of [Ni(alkynyl-cyclam)]$^{2+}$ catalysts to glassy carbon electrodes.

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Supporting Information

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1. GCEs modified with [Ni(pentynyl-cyclam)]$^{2+}$ and [Ni(hexynyl-cyclam)]$^{2+}$.

Cyclic voltammetry. Cyclic voltammetry experiments were performed using BASi Epsilon and Gamry Reference potentiostats. A single compartment cell was used in all experiments with GCE as a working electrode (3.0 mm diameter, surface area 0.071 cm^2), Pt wire as a counter and Ag/Ag+ with vycor tip as a reference electrode. All electrografting experiments were carried out in a glove box under an N_2 atmosphere. Electrochemical CO_2 reduction experiments were performed on a Schlenk line using N_2 or CO_2 gas. Solvents were taken from a solvent system distilled and stored under 3Å molecular sieves. All potentials were converted to the internal standard $Fc^{+/0}$. CVs were taken with the compensation for iR drop.

DPV experiments. DPV epxeriments were carried out to determine surface coverages of newly modified electrodes and were taken using BASi Epsilon potentiostat in 0.1 M $TBAPF_6$/DCM solution in a N_2 glovebox. The charge passed in uC units was determined automatically by the potentiostat.

All electrografting experiments including scan rate dependence studies were carried out in the N_2 glovebox in 0.1 M $TBAPF_6$ solution in DCM at various scan rates with mod-GCE as a working electrode, Ag wire in the glass tube with vycor tip as a reference and Pt wire as a counter electrode. All experiments were carried out with iR-drop compensation.

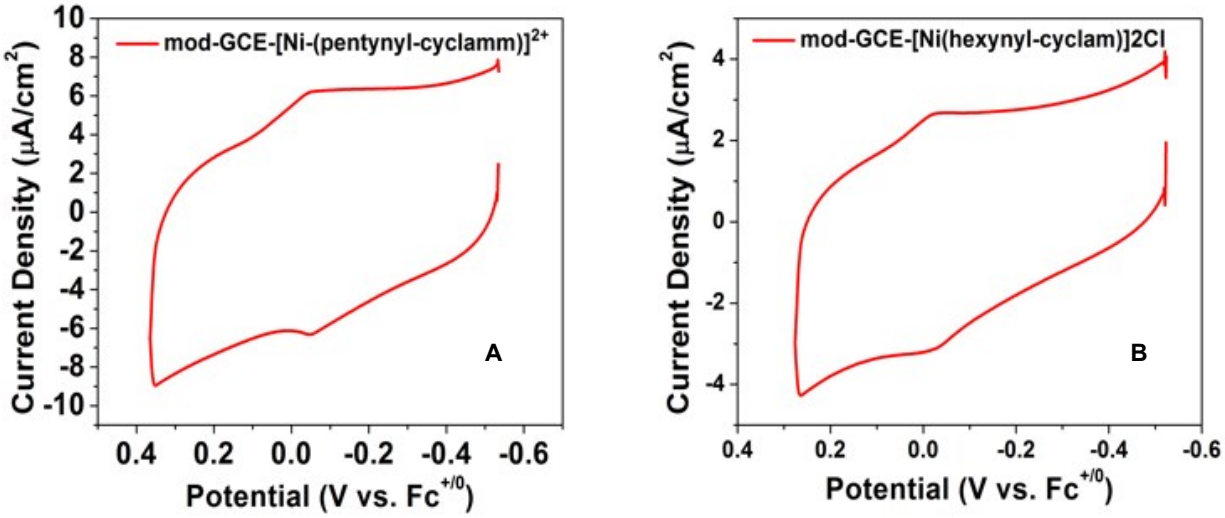


Fig. S1. CV of mod-GCE-2 **(A)** and mod-GCE-3 **(B)** in 0.1 M $TBAPF_6$ in DCM. Scan rate 50 mv/s.

2. Homogeneous catalysis with [Ni(hexynyl-cyclam)]$^{2+}$.

CO_2 reduction studies were carried out in the N_2 and CO_2 atmosphere in 0.1 M $TBAPF_6$ solution in MeCN. GCE used as a working electrode, Ag wire in the glass tube with vycor tip as a reference and Pt wire as a counter electrode. All experiments were carried out with iR-drop compensation. Catalytic current enhancement was observed with 1mM [Ni(alkynyl cyclam)]$^{2+}$ catalysts in MeCN under CO_2 atmosphere in the presence of 20% water as a proton source.

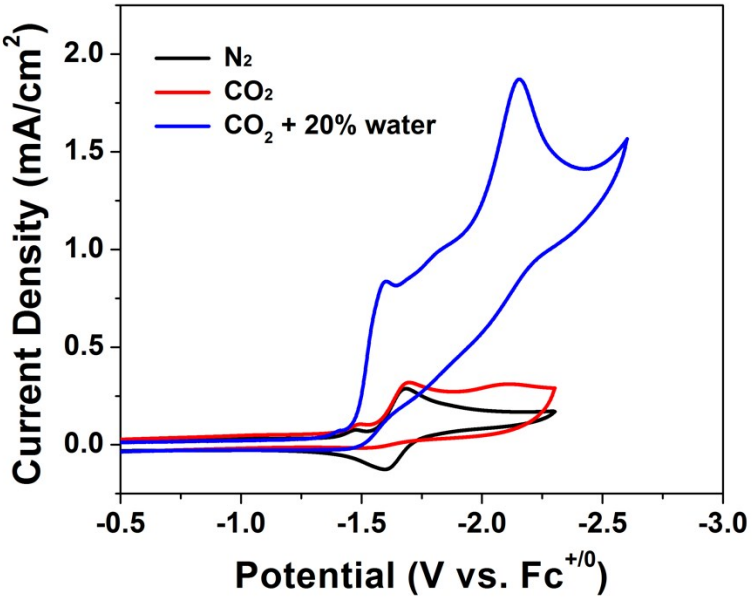
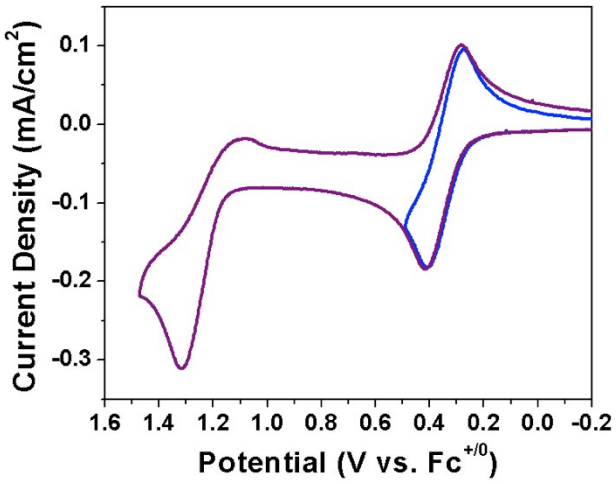


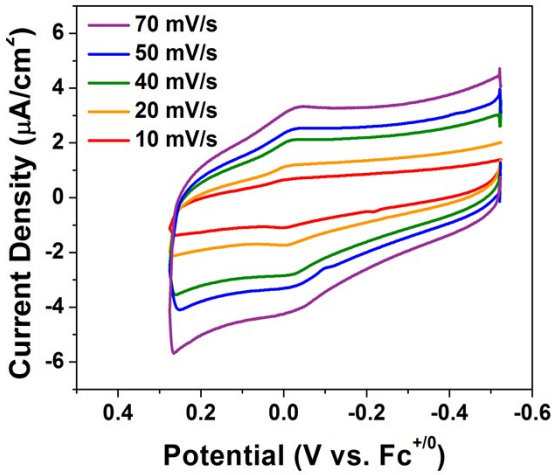
Fig. S2. Homogeneous electrocatalysis with 1 mM complex **3** under in 0.1 M TBAPF/MeCN with 20% water

3. Cyclic voltammetry of [Ni(hexynyl-cyclam)]$^{2+}$and mod-GCE-3.



Scan rate 200 mv/s.

Figure S3b. CV of Complex **3** in 0.1 M $TBAPF_6$ in DCM.



g. S4 Scan rate studies of **mod-GCE-3** in 0.1 M $TBAPF_6$ in DCM at various scan rates.

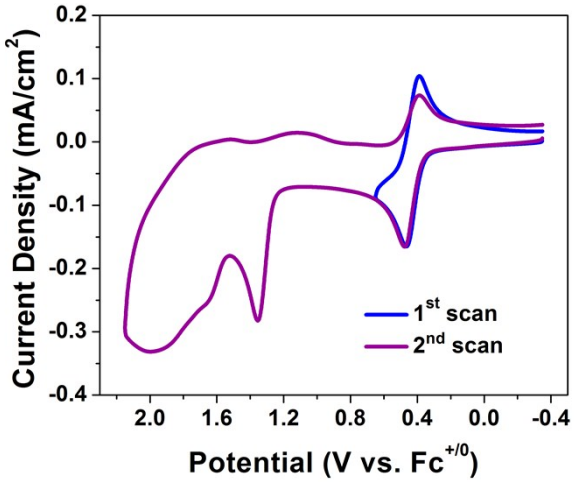


Fig. S5 CV of 0.5 mM complex **2** in 0.1 M $TBAPF_6$ in DCM. Scan rate 100 mv/s.

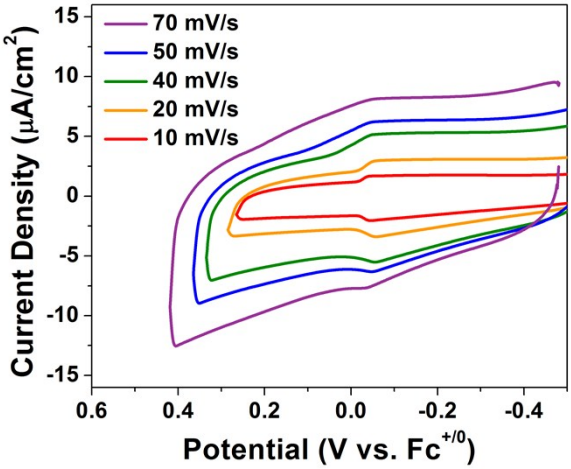


Fig. S6 Scan rate of **mod-GCE-2** in 0.1 M $TBAPF_6$ in DCM at various scan rates.

4. Cyclic voltammetry of $[Ni(pentynyl\text{-}cyclam)]^{2+}$ and mod-GCE-2.

5. Table S1. Redox potentials ($Ni^{III/II}$) of complexes 1, 2, 3 in solution and surface attached to GCE.

Complex	$\Delta E_{1/2}$ homogeneous	$\Delta E_{1/2}$ attached	ΔE
1	+0.35	-0.10	0.45
2	+0.38	-0.04	0.42
3	+0.35	-0.03	0.38

*all potentials are referenced to V vs. $Fc^{+/0}$.

6. Scan rate dependence studies of [Ni(alkynyl-cyclams)]$^{2+}$

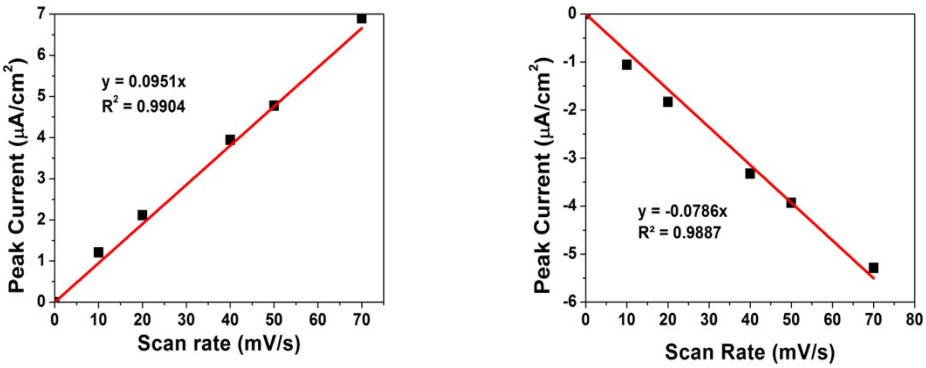


Fig. S7 Scan rate dependence of **mod-GCE-1**

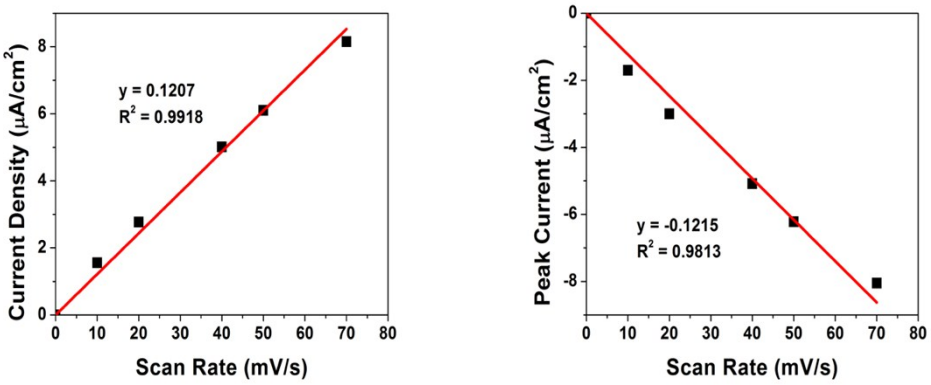


Fig. S8 Scan rate dependence of **mod-GCE-2**.

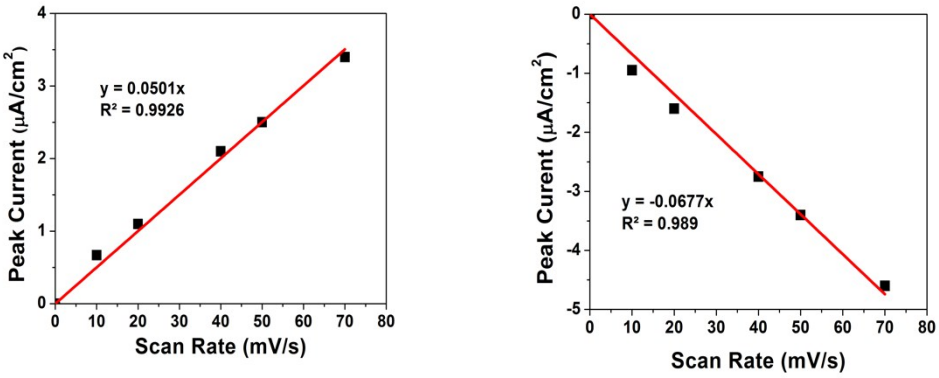


Fig. S9 Scan rate dependence of **mod-GCE-3**.

7. Surface coverage determination:

Theoretical surface coverage

Theoretical surface coverages of the modified electrodes were calculated according to the approximation that each molecule considered to be a circular "tile" with the corresponding diameter (d), assuming that these molecules are close packed within a monolayer forming a tile mosaic on the surface of a GCE.

Theoretical surface coverage of Fc is 4.5 x 10^{-10} mol/cm^2.
Diameter of Fc d = 6 Å
Size of Ni-C_3-cyclam: distance from C_1 to the furthest carbon atom considered as a diameter **d** = 8.13 Å.

Ni-C_5-cyclam **d** = 10.36 Å
Ni-C_6-cyclam **d** = 11.23 Å.

Ni-C_3-cyclam $\frac{6^2 * 4.5 * 10^{-10}}{8.13^2} = 2.53 * 10^{-10} mol/cm^2$

Ni-C_5-cyclam $\frac{6^2 * 4.5 * 10^{-10}}{10.01^2} = 1.62 * 10^{-10} mol/cm^2$

Ni-C_6-cyclam $\frac{6^2 * 4.5 * 10^{-10}}{11^2} = 1.28 * 10^{-10} mol/cm^2$

Experimental surface coverage

DPV studies were carried in 0.1 M $TBAPF_6$ solution in dry DCM with Mod-GCE as a working electrode, Pt – counter, Ag wire as a reference. Charge passed was determined using the area under the peak current and was determined automatically using BASi Epsilon potentiostat.

Γ (**mod-GCE-3**) = 0.88 (uC)*10^{-6}/ 96485.3365 (C/mol) x 0.071 (cm^2) = 1.28*10^{-10} mol/cm^2.
Γ (**mod-GCE-2**) = 1.02 (uC)*10^{-6}/ 96485.3365 (C/mol) x 0.071 (cm^2) = 1.46*10^{-10} mol/cm^2.
Γ (**mod-GCE-1**) = 1.54 (uC)*10^{-6}/ 96485.3365 (C/mol) x 0.071 (cm^2) = 2.25*10^{-10} mol/cm^2.

8. Electrografting.

Anodic electrografting were performed using cyclic voltammetry with 0.5 mM Ni-alkynyl-cyclam catalyst in 0.1 M $TBAPF_6$/DCM solution with 10 consecutive anodic scans. The decrease in current during electrografting indicated of the absence of a polymer film formation at the surface of the electrode. The increase in peak current would be detected otherwise.

The purity and dryness of solvents affect eletcrografting process. Therefore, all solvents were taken from the solvents system, distilled and stored under 3Å molecular sieves in the glovebox.

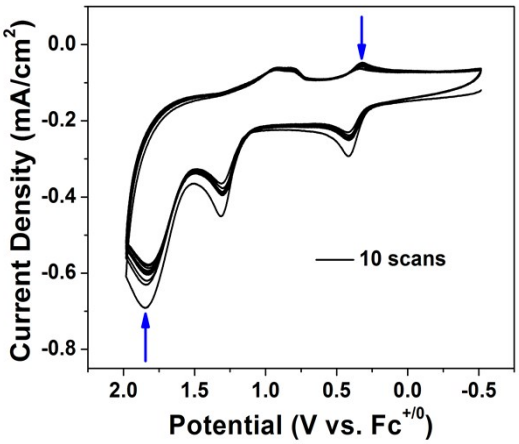


Fig. S10. CV of 0.5 mM [Ni(hexynyl-cyclam)]2Cl in 0.1 M $TBAPF_6$ in DCM. 10 scans. Scan rate 200

9. Controlled Potential Electrolysis.

CPE experiments were carried out using Gamry Potentiostat. A one compartment cell was used with blank and modified Tokai glassy carbon electrodes with the fixed surface area of 2 cm^2. Platinum wire was used as a counter electrode, and a Ag/AgCl in a glass tube with vycor tip as a reference electrode. Gas analysis for CPE were performed using 1 mL sample taken from the headspace of the electrochemical cell and injected on a Hewlett-Packard 7890A Series gas chromatograph with a column (30 m x 0.53 mm ID x 25 µm film).

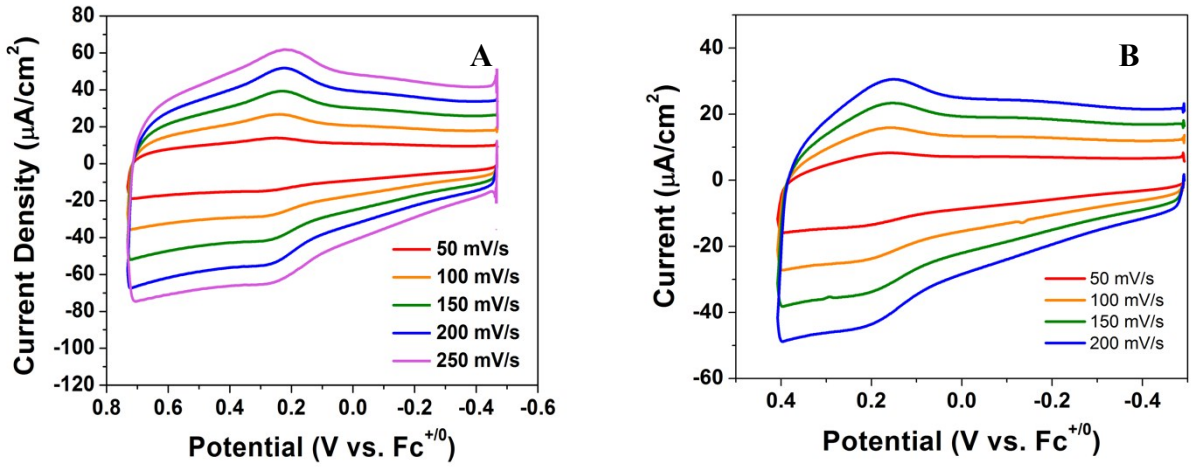


Figure S11. Tokai GCE electrodes modified with Ni-alkynyl cyclams. CVs in 0.1 M $TBAPF_6$ in DCM for the electrode modified with complex **2** mod-GCE-2 (**A**) and with complex **3** GCE-mod-3 (**B**).

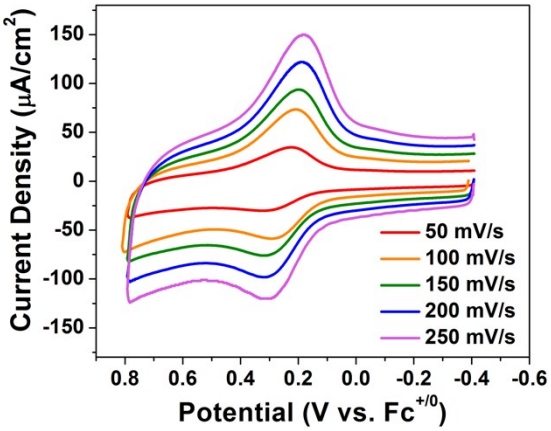


Figure S12. Carbon cloth electrode modified with complex **3**.
CV in 0.1 M TBAPF6 in DCM.

Table S2. Results of CPE of Nickel alkynyl cyclams modified electrodes in MeCN/20% H_2O solution.

	Faradaic efficiency, % H_2	Faradaic efficiency, % CO
GCE-mod-1	87	7
GCE-mod-2	89	8
GCE-mod-3	91	7

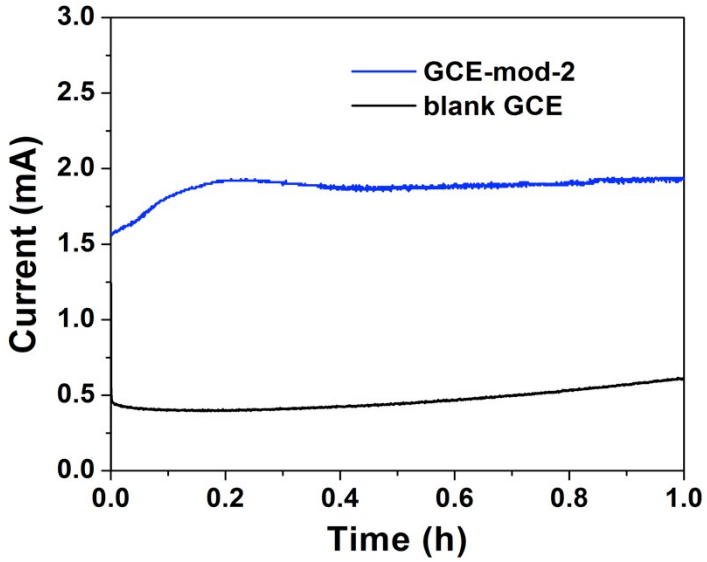


Figure S13. Controlled potential electrolysis of mod-GCE-2 (blue) and blank GCE (black) in CO_2 saturated solution of 0.1 M $TBAPF_6$/MeCN with 20% water.

10.Synthesis and characterization of Ni-alkynyl-cyclams.

NMR spectra were recorded on a Varian 400 MHz spectrometer at 298 K, and data were manipulated using ACD/NMR Processor Academic Edition software. ^{1}H chemical shifts are reported relative to TMS ($\delta = 0$) and referenced against solvent residual peaks.

Microanalyses were performed by NuMega Resonance Lab (San Diego, CA) for C, H and N.

Tetrabutylammonium hexafluorophosphate ($TBAPF_6$, Sigma Aldrich, 98%) was twice recrystallized from methanol (MeOH) and dried under a vacuum at 90°C overnight before use.

Reagents for alkynyl-cyclams synthesis were used as received: 1,4,8,11-tetraazacyclotetradecane (Sigma Aldrich, > 98%), 5-iodo-1-pentyne (Sigma Aldrich, > 98%), 6-iodo-1-hexyne (Sigma Aldrich, > 97%), propargyl bromide solution (Sigma Aldrich, 80 wt. % in toluene).

1,4,8-Tris(tert-butoxycarbonyl)-1,4,8,11-tetraazacyclotetradecane. Synthesis of Tri(N-Boc)cyclam was similar to a previously described procedure[1]. To a solution of cyclam (1 g, 5 mmol) in dry dichloromethane (500 ml) triethylamine (25 mmol) was added under N_2 atmosphere. Di-*tert*-butyl-bicarbonate (1.96 g, 9 mmol) was dissolved in 60 ml of dichloromethane and was added dropwise to a reaction mixture. The solution was stirred and cooled to -15 °C using ice/NaCl (3:1) mixture. Another portion of di-*tert*-butyl-bicarbonate (1.31 g, 6 mmol) was added and the mixture was stirred at room temperature for 18 hours. Extraction and purification was performed using 400 ml of 0.5 N Na_2CO_3 and organic solution was dried over $MgSO_4$. The product was concentrated under reduced pressure and purified by flash column chromatography (silica gel, ethyl acetate/methanol 9:1). Excess solvent was removed in vacuo and a colorless liquid of a tri(N-Boc) protected cyclam was obtained in a 70% yield. ^{1}H NMR (400 MHz, CDCl3): δ = 3.29 (m, 12H; CH_2), 2.77 (t, 2H; CH_2), 2.60 (t, 2H; CH_2), 1.92 (q, 2H; CH_2), 1.70 (q, 2H; CH_2), 1.45 (s, 27H; $C(CH_3)_3$).

11-Prop-2-ynyl-1,4,8,11-tetraazacyclotetradecane-1,4,8-tricarboxylic acid tri-tert-butyl ester was adapted from a procedure[2]. Propargyl bromide (67 mL, 0.60 mmol) was added to a solution of tri(N-Boc)cyclam (250 mg, 0.50 mmol) and Na_2CO_3 (212 mg, 1 mmol) in dry acetonitrile (15 ml) under nitrogen atmosphere. The mixture was heated under reflux for 18 hours. The precipitate was filtered off and the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, Et_2OAc/hexane (7:3) to give the desired product in 70% yield. ^{1}H MNR ($CDCl_3$, 400 MHz): δ = 3.48–3.20 (m, 14H), 2.67 (m, 2H), 2.51 (t, J=5.4 Hz, 2H), 2.16 (s, 1 H), 1.88 (m, 2H), 1.69 (m, 2H), 1.46 ppm (s, 27H); HRMS (ES): *m/z*: 539.38 $[M+H]^+$.

11-Prop-2-ynyl-1,4,8,11-tetraaza-cyclotetradecane. Deprotection was performed according to a general synthetic procedure adapted from a previous report[3]. Compound **2** was dissolved in a mixture of TFA/DCM/H_2O (90:5:5 5mM) and the reaction mixture was stirred at room temperature for 6 h. The solvent and the excess of TFA/DCM/H_2O was removed *in vacuo* to give the desired product as a trifluoroacetate salt. ^{1}H MNR ($CDCl_3$, 400 MHz): δ = 3.39 (s, 2H), 2.95 (m, 4H), 2.86 (m, 4H), 2.72 (m, 4 H), 2.52 (m, 4H), 2.20 (s, 1H), 1.94 (m, 2H), 1.66 (m, 2H); HRMS (ES): *m/z*: 239.44 $[M+H]^+$. The trifluoroacetate salt was dissolved in 0.5 ml H_2O, basified with 2M NaOH to pH 11-12, and extracted with $CHCl_3$ (3x). The organic phases were collected, washed with 0.5 ml H_2O and concentrated under reduced pressure to give deprotected propargyl-

cyclam in 50% yield. ^{1}H MNR ($CDCl_3$, 400 MHz): δ = 3.50 (m, 2H), 2.72 (m, 4H), 2.64 (t, J=5.4 Hz, 12H), 2.14 (s, 1 H), 1.72 (m, 4H). ^{13}C NMR ($CDCl_3$, 400MHz) δ 77.61, 73.53, 54.01, 52.18, 50.89, 49.83, 49.61, 49.19, 48.8, 48.17, 46.8, 22.78, 22.77. HRMS (ES): *m/z*: 239.22 $[M+H]^+$.

Synthesis of 11-pent-2-ynyl-1,4,8,11-tetraaza-cyclotetradecane and 11-hex-2-ynyl-1,4,8,11-tetraaza-cyclotetradecane was carried out accordingly, using 1-5-iodo-1-pentyne and 6-iodo-1-hexyne.

11-pent-2-ynyl-1,4,8,11-tetraaza-cyclotetradecane. ^{1}HNMR ($CDCl_3$, 400 MHz): δ = 2.75 (m, 6H), 2.69 (m, 2H), 2.65 (m, 2H), 2.52 (m, 6H), 2.18 (s, 1H), 1.95 (m, 2H), 1.74 (m, 8H). ^{13}C NMR ($CDCl_3$, 400MHz) δ 84.4, 74.43, 54.67, 53.67, 51.65, 51.19, 49.55, 49.38, 49.02, 48.11, 47.76, 26.39, 22.8, 22.7, 16.4. HRMS (ES): *m/z*: 267.25 $[M+H]^+$.

11-hex-2-ynyl-1,4,8,11-tetraaza-cyclotetradecane. ^{1}HNMR ($CDCl_3$, 400 MHz): δ = 2.75 (m, 8H), 2.69 (m, 2H), 2.63 (m, 4H), 2.42 (m, 2H), 2.19 (s, 1H), 1.74 (m, 4H), 1.55 (m, 2H), 1.31 (m, 2H), 0.91 (m, 2H). ^{13}C NMR ($CDCl_3$, 400MHz) δ 74.54, 68.73, 55.69, 53.57, 52.78, 52.53, 50.74, 49.33, 49.24, 48.61, 47.27, 27.22, 26.53, 25.43, 25.08, 18.61. HRMS (ES): *m/z*: 281.27 $[M+H]^+$.

Metalation: Addition of 0.1 M solution of $NiCl_2 \cdot 6H_2O$ to an equivalent amount of N-functionalized cyclam in EtOH resulted in the formation of a purple precipitate at room temperature or at -20 °C. Crystals suitable for X-ray analysis were obtained in DCM/pentane through vapor diffusion crystallization.

Synthesis of [Ni-(propargyl-cyclam)]$^{2+}$ (1). 11-Prop-2-ynyl-1,4,8,11-tetraaza-cyclotetradecane (0.1M) was dissolved in EtOH and was slowly added to $NiCl_2$ x $6H_2O$ (0.1M) in EtOH at room temperature. Purple precipitate formed immediately and was recrystallized in DCM/pentane trough vapor diffusion crystallization to give complex **1** as purple crystals in 80% yield. HRMS (ES): *m/z*: 295.14 $[M-Cl]^+$. IR: ν =3217.4, 2918.8, 2856.9, 1458.3, 1418.2, 1109.7, 941.3, 675.7 755.8, 864.9. Anal. Cald. for complex **1**. $C_{13}H_{26}Cl_2N_4Ni$ + pentane: C, 49.12; H, 8.70; N, 12.73. Found: C, 48.43; H, 8.59; N 12.51.

Synthesis of [Ni-(pentynyl-cyclam)]$^{2+}$ (2). 11-pent-2-ynyl-1,4,8,11-tetraaza-cyclotetradecane was dissolved in minimal amount of EtOH and added to $NiCl_2$ x $6H_2O$ solution in EtOH. Solution changed color from green to purple immediately and was left for crystallization at -20 ^{o}C. Purple precipitate formed and was recrystallized in DCM/pentane trough vapor diffusion crystallization to give complex **2** in 50% yield. HRMS (ES): *m/z*: 323.17 $[M-Cl]^+$. IR: ν = 3210.6, 2924.8, 2854.1, 1456.1, 1100.6, 946.3, 585.1, 668.4, 721.1. Anal. Cald. for complex **2**. $C_{15}H_{32}Cl_2N_4NiO$ + pentane: C, 42.51; H, 7.79; N, 13.53. Found: C, 42.41; H, 7.29; N 13.29.

Synthesis of [Ni-(hexynyl-cyclam)]$^{2+}$ (3). The synthetic procedure for complex **3** is similar to the synthesis for complexes **1** and **2**. Dark purple solution formed immediately after addition of 11-hex-2-ynyl-1,4,8,11-tetraaza-cyclotetradecane to $NiCl_2$ x $6H_2O$ in EtOH and purple precipitate crashed out at -20 °C. Purple crystals suitable for X-ray analysis were obtained after recrystallization in DCM/pentane. Yield 60%. HRMS (ES): *m/z*: 337.19 $[M-Cl]^+$. IR: ν= 3218.5, 2931.3, 2968.2, 1465.5, 1426.7, 1099.5, 943.9, 668.5, 874.9. Anal. Cald. for complex **3**. $C_{16}H_{34}Cl_2N_4NiO$ + pentane: C, 44.89; H, 8.01; N, 13.09. Found: C, 44.40; H, 8.11; N 13.93.

Table S3. Elemental analysis.

	Experimental (%)	Theoretical (%)
[Ni(pentynyl-cyclam)]$(Cl)_2(H_2O)$ C15 H32 Cl_2 N4 Ni O, Ms = 414.039 g/mol		
C	42.41	42.51
H	8.29	7.79
N	13.29	13.53
[Ni(hexynyl-cyclam)]$(Cl)_2(H_2O)$ C16 H34 Cl2 N4 Ni O, Ms = 428.0.65 g/mol		
C	44.40	44.89
H	8.11	8.01
N	13.93	13.09
[Ni(propargyl-cyclam)]$(Cl)_2$ C13 H26 Cl2 N4 Ni + pentane. Ms = 440.119 g/mol		
C	48.43	49.12
H	8.59	8.70
N	12.51	12.73

11.Crystallography.

[Ni(propargyl-cyclam)]$^{2+}$

Experimental Summary

The single crystal X-ray diffraction studies were carried out on a Bruker Kappa APEX-II CCD diffractometer equipped with Cu K_α radiation (λ = 1.5478). A 0.217 x 0.053 x 0.041 mm piece of a light purple needle was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using ϕ and ϖ scans. Crystal-to-detector distance was 40 mm using variable exposure time (10s-20s) depending on θ□with a scan width of 1.0°. Data collection was 99.2% complete to 68.00° in θ. A total of 25028 reflections were collected covering the indices, -7<=h<=7, -17<=k<=17, -21<=l<=21. 3026 reflections were found to be symmetry independent, with a R_{int} of 0.0551. Indexing and unit cell refinement indicated a primitive, monoclinic lattice. The space group was found to be $P2_1/n$. The data were integrated using the Bruker SAINT software program and scaled using the SADABS software program. Solution by direct methods (SHELXT) produced a complete phasing model consistent with the proposed structure.

All nonhydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014. Crystallographic data are summarized in Table 1.

Table 1. Crystal data and structure refinement for AZ164.

Report date	2017-09-07	
Identification code	AZ164	
Empirical formula	C13 H26 Cl2 N4 Ni	
Molecular formula	C13 H26 Cl2 N4 Ni	
Formula weight	367.99	
Temperature	100.0 K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 6.5736(4) Å	□= 90°.
	b = 14.4609(7) Å	□= 91.312(4)°.
	c = 17.5037(9) Å	□ = 90°.
Volume	1663.47(16) $Å^3$	
Z	4	
Density (calculated)	1.469 Mg/m^3	
Absorption coefficient	4.597 mm^{-1}	
F(000)	776	
Crystal size	0.217 x 0.053 x 0.041 mm^3	
Crystal color, habit	Light Purple Needle	
Theta range for data collection	3.965 to 68.479°.	
Index ranges	-7<=h<=7, -17<=k<=17, -21<=l<=21	
Reflections collected	25028	
Independent reflections	3026 [R(int) = 0.0551, R(sigma) = 0.0298]	
Completeness to theta = 68.000°	99.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.3201 and 0.2167	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3026 / 0 / 181	
Goodness-of-fit on F^2	1.137	
Final R indices [I>2sigma(I)]	R1 = 0.0517, wR2 = 0.1218	
R indices (all data)	R1 = 0.0573, wR2 = 0.1242	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.600 and -0.341 e.$Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for AZ164. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ni(1)	5239(1)	7147(1)	3451(1)	25(1)
Cl(1)	2429(1)	6047(1)	3603(1)	31(1)
Cl(2)	8201(1)	8310(1)	3425(1)	33(1)
N(1)	5169(5)	7034(2)	2226(2)	31(1)
N(2)	3206(5)	8221(2)	3498(2)	32(1)
N(3)	5466(5)	7285(3)	4632(2)	34(1)
N(4)	7438(5)	6154(2)	3435(2)	27(1)
C(1)	5085(7)	7970(3)	1867(2)	37(1)
C(2)	3267(7)	8548(3)	2106(3)	42(1)
C(3)	3336(6)	8935(3)	2909(3)	39(1)
C(4)	3406(7)	8613(3)	4281(3)	43(1)
C(5)	3703(7)	7838(3)	4856(3)	42(1)
C(6)	5738(7)	6437(3)	5073(2)	41(1)
C(7)	7558(7)	5875(3)	4826(2)	41(1)
C(8)	7383(6)	5441(3)	4034(2)	36(1)
C(9)	7453(6)	5767(3)	2650(2)	36(1)
C(10)	7120(6)	6561(3)	2083(2)	36(1)
C(11)	3457(7)	6455(3)	1909(2)	39(1)
C(12)	3530(7)	6293(3)	1074(3)	41(1)
C(13)	3617(8)	6117(3)	418(3)	47(1)

Table 3. Bond lengths [Å] and angles [°] for AZ164.

Ni(1)-Cl(1)	2.4568(11)	C(7)-H(7A)	0.9900
Ni(1)-Cl(2)	2.5738(11)	C(7)-H(7B)	0.9900
Ni(1)-N(1)	2.149(3)	C(7)-C(8)	1.524(6)
Ni(1)-N(2)	2.051(3)	C(8)-H(8A)	0.9900
Ni(1)-N(3)	2.079(3)	C(8)-H(8B)	0.9900
Ni(1)-N(4)	2.039(3)	C(9)-H(9A)	0.9900
N(1)-C(1)	1.493(5)	C(9)-H(9B)	0.9900
N(1)-C(10)	1.480(5)	C(9)-C(10)	1.529(6)
N(1)-C(11)	1.498(5)	C(10)-H(10A)	0.9900
N(2)-H(2)	1.0000	C(10)-H(10B)	0.9900
N(2)-C(3)	1.464(5)	C(11)-H(11A)	0.9900
N(2)-C(4)	1.487(6)	C(11)-H(11B)	0.9900
N(3)-H(3)	1.0000	C(11)-C(12)	1.482(6)
N(3)-C(5)	1.469(6)	C(12)-C(13)	1.179(7)
N(3)-C(6)	1.459(6)	C(13)-H(13)	0.9500
N(4)-H(4)	1.0000		
N(4)-C(8)	1.472(5)	Cl(1)-Ni(1)-Cl(2)	174.77(4)
N(4)-C(9)	1.483(5)	N(1)-Ni(1)-Cl(1)	93.44(9)
C(1)-H(1A)	0.9900	N(1)-Ni(1)-Cl(2)	91.79(9)
C(1)-H(1B)	0.9900	N(2)-Ni(1)-Cl(1)	89.65(10)
C(1)-C(2)	1.525(6)	N(2)-Ni(1)-Cl(2)	89.99(10)
C(2)-H(2A)	0.9900	N(2)-Ni(1)-N(1)	95.67(13)
C(2)-H(2B)	0.9900	N(2)-Ni(1)-N(3)	85.38(14)
C(2)-C(3)	1.511(7)	N(3)-Ni(1)-Cl(1)	89.49(10)
C(3)-H(3A)	0.9900	N(3)-Ni(1)-Cl(2)	85.28(10)
C(3)-H(3B)	0.9900	N(3)-Ni(1)-N(1)	176.89(14)
C(4)-H(4A)	0.9900	N(4)-Ni(1)-Cl(1)	94.60(9)
C(4)-H(4B)	0.9900	N(4)-Ni(1)-Cl(2)	85.60(9)
C(4)-C(5)	1.515(7)	N(4)-Ni(1)-N(1)	86.07(13)
C(5)-H(5A)	0.9900	N(4)-Ni(1)-N(2)	175.31(13)
C(5)-H(5B)	0.9900	N(4)-Ni(1)-N(3)	92.66(14)
C(6)-H(6A)	0.9900	C(1)-N(1)-Ni(1)	110.5(3)
C(6)-H(6B)	0.9900	C(1)-N(1)-C(11)	109.3(3)
C(6)-C(7)	1.517(7)	C(10)-N(1)-Ni(1)	101.8(2)

C(10)-N(1)-C(1)	111.8(3)	C(2)-C(3)-H(3A)	109.0
C(10)-N(1)-C(11)	109.0(3)	C(2)-C(3)-H(3B)	109.0
C(11)-N(1)-Ni(1)	114.2(2)	H(3A)-C(3)-H(3B)	107.8
Ni(1)-N(2)-H(2)	106.9	N(2)-C(4)-H(4A)	109.7
C(3)-N(2)-Ni(1)	117.2(3)	N(2)-C(4)-H(4B)	109.7
C(3)-N(2)-H(2)	106.9	N(2)-C(4)-C(5)	109.8(4)
C(3)-N(2)-C(4)	112.1(3)	H(4A)-C(4)-H(4B)	108.2
C(4)-N(2)-Ni(1)	106.4(3)	C(5)-C(4)-H(4A)	109.7
C(4)-N(2)-H(2)	106.9	C(5)-C(4)-H(4B)	109.7
Ni(1)-N(3)-H(3)	106.4	N(3)-C(5)-C(4)	108.4(3)
C(5)-N(3)-Ni(1)	106.2(3)	N(3)-C(5)-H(5A)	110.0
C(5)-N(3)-H(3)	106.4	N(3)-C(5)-H(5B)	110.0
C(6)-N(3)-Ni(1)	116.8(3)	C(4)-C(5)-H(5A)	110.0
C(6)-N(3)-H(3)	106.4	C(4)-C(5)-H(5B)	110.0
C(6)-N(3)-C(5)	113.8(3)	H(5A)-C(5)-H(5B)	108.4
Ni(1)-N(4)-H(4)	106.1	N(3)-C(6)-H(6A)	109.0
C(8)-N(4)-Ni(1)	117.0(2)	N(3)-C(6)-H(6B)	109.0
C(8)-N(4)-H(4)	106.1	N(3)-C(6)-C(7)	112.8(3)
C(8)-N(4)-C(9)	113.4(3)	H(6A)-C(6)-H(6B)	107.8
C(9)-N(4)-Ni(1)	107.3(2)	C(7)-C(6)-H(6A)	109.0
C(9)-N(4)-H(4)	106.1	C(7)-C(6)-H(6B)	109.0
N(1)-C(1)-H(1A)	108.8	C(6)-C(7)-H(7A)	108.3
N(1)-C(1)-H(1B)	108.8	C(6)-C(7)-H(7B)	108.3
N(1)-C(1)-C(2)	113.8(3)	C(6)-C(7)-C(8)	115.9(3)
H(1A)-C(1)-H(1B)	107.7	H(7A)-C(7)-H(7B)	107.4
C(2)-C(1)-H(1A)	108.8	C(8)-C(7)-H(7A)	108.3
C(2)-C(1)-H(1B)	108.8	C(8)-C(7)-H(7B)	108.3
C(1)-C(2)-H(2A)	108.1	N(4)-C(8)-C(7)	111.0(3)
C(1)-C(2)-H(2B)	108.1	N(4)-C(8)-H(8A)	109.4
H(2A)-C(2)-H(2B)	107.3	N(4)-C(8)-H(8B)	109.4
C(3)-C(2)-C(1)	116.8(4)	C(7)-C(8)-H(8A)	109.4
C(3)-C(2)-H(2A)	108.1	C(7)-C(8)-H(8B)	109.4
C(3)-C(2)-H(2B)	108.1	H(8A)-C(8)-H(8B)	108.0
N(2)-C(3)-C(2)	113.1(3)	N(4)-C(9)-H(9A)	110.0
N(2)-C(3)-H(3A)	109.0	N(4)-C(9)-H(9B)	110.0
N(2)-C(3)-H(3B)	109.0	N(4)-C(9)-C(10)	108.3(3)

H(9A)-C(9)-H(9B)	108.4
C(10)-C(9)-H(9A)	110.0
C(10)-C(9)-H(9B)	110.0
N(1)-C(10)-C(9)	110.5(3)
N(1)-C(10)-H(10A)	109.6
N(1)-C(10)-H(10B)	109.6
C(9)-C(10)-H(10A)	109.6
C(9)-C(10)-H(10B)	109.6
H(10A)-C(10)-H(10B)	108.1
N(1)-C(11)-H(11A)	108.7
N(1)-C(11)-H(11B)	108.7
H(11A)-C(11)-H(11B)	107.6
C(12)-C(11)-N(1)	114.4(4)
C(12)-C(11)-H(11A)	108.7
C(12)-C(11)-H(11B)	108.7
C(13)-C(12)-C(11)	176.5(5)
C(12)-C(13)-H(13)	180.0

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for AZ164. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ni(1)	22(1)	27(1)	26(1)	3(1)	0(1)	2(1)
Cl(1)	24(1)	29(1)	41(1)	3(1)	-1(1)	-3(1)
Cl(2)	24(1)	32(1)	42(1)	1(1)	-1(1)	-2(1)
N(1)	32(2)	34(2)	26(2)	6(1)	-1(1)	0(1)
N(2)	20(2)	29(2)	48(2)	1(2)	-1(1)	1(1)
N(3)	31(2)	45(2)	28(2)	1(2)	1(1)	-7(2)
N(4)	23(2)	24(2)	34(2)	3(1)	-1(1)	2(1)
C(1)	42(2)	34(2)	33(2)	12(2)	-5(2)	-9(2)
C(2)	36(2)	33(2)	57(3)	20(2)	-9(2)	-4(2)
C(3)	29(2)	28(2)	60(3)	9(2)	-3(2)	2(2)
C(4)	32(2)	43(3)	54(3)	-16(2)	9(2)	1(2)
C(5)	40(2)	49(3)	39(2)	-13(2)	11(2)	-8(2)
C(6)	43(2)	57(3)	24(2)	7(2)	-1(2)	-13(2)
C(7)	37(2)	46(3)	39(2)	18(2)	-10(2)	-10(2)
C(8)	28(2)	33(2)	46(2)	14(2)	-3(2)	0(2)
C(9)	31(2)	37(2)	41(2)	-8(2)	-1(2)	6(2)
C(10)	32(2)	47(2)	30(2)	-2(2)	3(2)	-1(2)
C(11)	40(2)	39(2)	38(2)	1(2)	0(2)	-3(2)
C(12)	42(3)	39(2)	43(3)	4(2)	-5(2)	-3(2)
C(13)	51(3)	48(3)	43(3)	-1(2)	-5(2)	3(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for AZ164.

	x	y	z	U(eq)
H(2)	1814	7945	3450	39
H(3)	6697	7674	4741	41
H(4)	8763	6485	3510	33
H(1A)	5033	7897	1305	44
H(1B)	6351	8307	2004	44
H(2A)	3119	9072	1745	51
H(2B)	2029	8163	2049	51
H(3A)	4620	9284	2987	47
H(3B)	2195	9375	2966	47
H(4A)	2166	8968	4401	51
H(4B)	4583	9039	4310	51
H(5A)	3941	8099	5374	51
H(5B)	2471	7445	4866	51
H(6A)	4495	6054	5017	50
H(6B)	5914	6597	5621	50
H(7A)	7795	5374	5204	49
H(7B)	8771	6281	4843	49
H(8A)	8519	5001	3966	43
H(8B)	6092	5091	3987	43
H(9A)	6359	5302	2585	44
H(9B)	8774	5462	2558	44
H(10A)	8253	7009	2136	44
H(10B)	7108	6316	1555	44
H(11A)	3475	5850	2173	47
H(11B)	2154	6762	2025	47
H(13)	3687	5975	-110	57

Table 6. Hydrogen bonds for AZ164 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(2)-H(2)...Cl(2)#1	1.00	2.43	3.293(3)	143.8
N(4)-H(4)...Cl(1)#2	1.00	2.49	3.291(3)	136.5

Symmetry transformations used to generate equivalent atoms:

#1 x-1,y,z #2 x+1,y,z

[Ni(pentynyl-cyclam)]$^{2+}$

Experimental Summary

The single crystal X-ray diffraction studies were carried out on a Bruker Kappa APEX-II CCD diffractometer equipped with Cu K_α radiation (λ = 1.5478). A 0.217 x 0.053 x 0.041 mm piece of a light purple needle was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using ϕ and ϖ scans. Crystal-to-detector distance was 40 mm using variable exposure time (10s-20s) depending on θ with a scan width of 1.0°. Data collection was 99.2% complete to 68° in θ. A total of 19269 reflections were collected covering the indices, -10<=h<=10, -14<=k<=15, -15<=l<=15. 4584 reflections were found to be symmetry independent, with a R_{int} of 0.0551. Indexing and unit cell refinement indicated a triclinic lattice. The space group was found to be *P*-1. The data were integrated using the Bruker SAINT software program and scaled using the SADABS software program. Solution by direct methods (SHELXT) produced a complete phasing model consistent with the proposed structure.

All nonhydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014. Crystallographic data are summarized in Table 1.

Table 1. Crystal data and structure refinement for AZ193.

Report date	2017-08-07	
Identification code	AZ193	
Empirical formula	C15 H32 Cl N4 Ni O, Cl, C H2 Cl2	
Molecular formula	C16 H34 Cl4 N4 Ni O	
Formula weight	498.98	
Temperature	100.0 K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 8.4321(6) Å	□= 106.833 (2)°
	b = 12.0889(8) Å	□= 100.100 (3)°
	c = 12.5339(9) Å	□ = 107.515 (2)°
Volume	1116.93(14) $Å^3$	
Z	2	
Density (calculated)	1.469 Mg/m^3	
Absorption coefficient	1.361 mm^{-1}	
F(000)	524	
Crystal size	0.05 x 0.01 x 0.01 mm^3	
Crystal color, habit	Light Purple Needle	
Theta range for data collection	1.772 to 26.487°.	
Index ranges	-10<=h<=10, -14<=k<=15, -15<=l<=15	
Reflections collected	19269	
Independent reflections	4584 [R(int) = 0.0364, R(sigma) = 0.0340]	
Completeness to theta = 68.000°	100 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.0932 and 0.0664	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4584 / 2 / 241	
Goodness-of-fit on F^2	1.030	
Final R indices [I>2sigma(I)]	R1 = 0.0300, wR2 = 0.0669	
R indices (all data)	R1 = 0.0399, wR2 = 0.0714	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.604 and -0.667 $e.Å^{-3}$	

	x	*y*	*z*	U_{iso}*/U_{eq}
Ni1	0.81684 (3)	0.71789 (2)	0.79718 (2)	0.01139 (8)
Cl1	1.07736 (6)	0.85152 (5)	0.97099 (4)	0.01491 (12)
O1	0.57368 (19)	0.59225 (14)	0.66653 (13)	0.0154 (3)
N1	0.9438 (2)	0.77153 (16)	0.67560 (14)	0.0135 (4)
N2	0.7540 (2)	0.87229 (16)	0.81906 (14)	0.0137 (4)
N3	0.6931 (2)	0.66891 (16)	0.91600 (15)	0.0144 (4)
N4	0.8849 (2)	0.56517 (16)	0.78378 (14)	0.0138 (4)
C1	0.9603 (3)	0.7434 (2)	0.19204 (19)	0.0229 (5)
C2	0.8827 (3)	0.7141 (2)	0.25537 (18)	0.0193 (5)
C3	0.7985 (3)	0.6817 (2)	0.34168 (18)	0.0172 (5)
C4	0.9311 (3)	0.7318 (2)	0.46128 (18)	0.0181 (5)
C5	0.8405 (3)	0.7015 (2)	0.55096 (17)	0.0155 (4)
C6	0.9638 (3)	0.90476 (19)	0.70946 (18)	0.0154 (4)
C7	0.7961 (3)	0.9193 (2)	0.72739 (18)	0.0164 (4)
C8	0.5793 (3)	0.8624 (2)	0.83070 (18)	0.0163 (4)
C9	0.5458 (3)	0.8210 (2)	0.93118 (18)	0.0172 (5)
C10	0.5272 (3)	0.6872 (2)	0.91438 (19)	0.0175 (5)
C11	0.6795 (3)	0.5405 (2)	0.89984 (19)	0.0171 (5)
C12	0.8480 (3)	0.5269 (2)	0.88154 (18)	0.0164 (4)
C13	1.0656 (3)	0.5842 (2)	0.78031 (18)	0.0165 (4)
C14	1.1053 (3)	0.6270 (2)	0.68122 (18)	0.0169 (5)
C15	1.1164 (3)	0.7593 (2)	0.69629 (18)	0.0159 (4)
Cl2	0.36953 (6)	0.64940 (5)	0.47205 (4)	0.01787 (12)
Cl3	0.68428 (9)	0.96632 (7)	0.43987 (6)	0.04235 (19)
Cl4	0.47137 (11)	0.81518 (7)	0.20051 (6)	0.04625 (19)
C16	0.4721 (3)	0.8784 (3)	0.3463 (2)	0.0330 (6)

Table 3. Geometric parameters. Bond lengths [Å] and angles [°]

Ni1—Cl1	2.5157 (6)	C6—H6A	0.9900
Ni1—O1	2.1679 (15)	C6—H6B	0.9900
Ni1—N1	2.1483 (17)	C6—C7	1.523 (3)
Ni1—N2	2.0469 (18)	C7—H7A	0.9900
Ni1—N3	2.0838 (17)	C7—H7B	0.9900
Ni1—N4	2.0634 (18)	C8—H8A	0.9900
O1—H1A	0.828 (16)	C8—H8B	0.9900
O1—H1B	0.809 (16)	C8—C9	1.524 (3)
N1—C5	1.493 (3)	C9—H9A	0.9900
N1—C6	1.489 (3)	C9—H9B	0.9900
N1—C15	1.492 (3)	C9—C10	1.524 (3)
N2—H2	1.0000	C10—H10A	0.9900

N2—C7	1.473 (3)	C10—H10B	0.9900
N2—C8	1.478 (3)	C11—H11A	0.9900
N3—H3	1.0000	C11—H11B	0.9900
N3—C10	1.478 (3)	C11—C12	1.527 (3)
N3—C11	1.472 (3)	C12—H12A	0.9900
N4—H4	1.0000	C12—H12B	0.9900
N4—C12	1.479 (3)	C13—H13A	0.9900
N4—C13	1.482 (3)	C13—H13B	0.9900
C1—H1	0.9500	C13—C14	1.528 (3)
C1—C2	1.178 (3)	C14—H14A	0.9900
C2—C3	1.475 (3)	C14—H14B	0.9900
C3—H3A	0.9900	C14—C15	1.527 (3)
C3—H3B	0.9900	C15—H15A	0.9900
C3—C4	1.531 (3)	C15—H15B	0.9900
C4—H4A	0.9900	Cl3—C16	1.762 (3)
C4—H4B	0.9900	Cl4—C16	1.762 (3)
C4—C5	1.534 (3)	C16—H16A	0.9900
C5—H5A	0.9900	C16—H16B	0.9900
C5—H5B	0.9900		
O1—Ni1—Cl1	170.94 (4)	N1—C6—C7	110.37 (16)
N1—Ni1—Cl1	94.11 (5)	H6A—C6—H6B	108.1
N1—Ni1—O1	94.91 (6)	C7—C6—H6A	109.6
N2—Ni1—Cl1	87.07 (5)	C7—C6—H6B	109.6
N2—Ni1—O1	94.34 (6)	N2—C7—C6	108.54 (17)
N2—Ni1—N1	86.01 (7)	N2—C7—H7A	110.0
N2—Ni1—N3	92.97 (7)	N2—C7—H7B	110.0
N2—Ni1—N4	177.22 (7)	C6—C7—H7A	110.0
N3—Ni1—Cl1	85.67 (5)	C6—C7—H7B	110.0
N3—Ni1—O1	85.32 (6)	H7A—C7—H7B	108.4
N3—Ni1—N1	178.97 (7)	N2—C8—H8A	109.3
N4—Ni1—Cl1	90.63 (5)	N2—C8—H8B	109.3
N4—Ni1—O1	87.68 (6)	N2—C8—C9	111.45 (17)
N4—Ni1—N1	95.73 (7)	H8A—C8—H8B	108.0
N4—Ni1—N3	85.28 (7)	C9—C8—H8A	109.3
Ni1—O1—H1A	122.0 (18)	C9—C8—H8B	109.3
Ni1—O1—H1B	112.1 (18)	C8—C9—H9A	108.3
H1A—O1—H1B	104 (2)	C8—C9—H9B	108.3

C5—N1—Ni1	114.34 (12)	C8—C9—C10	115.83 (17)
C6—N1—Ni1	101.23 (11)	H9A—C9—H9B	107.4
C6—N1—C5	110.14 (16)	C10—C9—H9A	108.3
C6—N1—C15	111.09 (16)	C10—C9—H9B	108.3
C15—N1—Ni1	109.25 (12)	N3—C10—C9	112.24 (17)
C15—N1—C5	110.49 (16)	N3—C10—H10A	109.2
Ni1—N2—H2	105.7	N3—C10—H10B	109.2
C7—N2—Ni1	107.41 (12)	C9—C10—H10A	109.2
C7—N2—H2	105.7	C9—C10—H10B	109.2
C7—N2—C8	113.34 (16)	H10A—C10—H10B	107.9
C8—N2—Ni1	118.03 (13)	N3—C11—H11A	109.9
C8—N2—H2	105.7	N3—C11—H11B	109.9
Ni1—N3—H3	106.6	N3—C11—C12	108.98 (17)
C10—N3—Ni1	116.64 (13)	H11A—C11—H11B	108.3
C10—N3—H3	106.6	C12—C11—H11A	109.9
C11—N3—Ni1	106.20 (12)	C12—C11—H11B	109.9
C11—N3—H3	106.6	N4—C12—C11	109.51 (17)
C11—N3—C10	113.65 (16)	N4—C12—H12A	109.8
Ni1—N4—H4	107.6	N4—C12—H12B	109.8
C12—N4—Ni1	106.71 (12)	C11—C12—H12A	109.8
C12—N4—H4	107.6	C11—C12—H12B	109.8
C12—N4—C13	111.89 (16)	H12A—C12—H12B	108.2
C13—N4—Ni1	115.18 (13)	N4—C13—H13A	109.2
C13—N4—H4	107.6	N4—C13—H13B	109.2
C2—C1—H1	180.0	N4—C13—C14	111.96 (17)
C1—C2—C3	175.6 (2)	H13A—C13—H13B	107.9
C2—C3—H3A	109.5	C14—C13—H13A	109.2
C2—C3—H3B	109.5	C14—C13—H13B	109.2
C2—C3—C4	110.92 (18)	C13—C14—H14A	108.4
H3A—C3—H3B	108.0	C13—C14—H14B	108.4
C4—C3—H3A	109.5	H14A—C14—H14B	107.5
C4—C3—H3B	109.5	C15—C14—C13	115.48 (17)
C3—C4—H4A	109.6	C15—C14—H14A	108.4
C3—C4—H4B	109.6	C15—C14—H14B	108.4
C3—C4—C5	110.28 (17)	N1—C15—C14	113.61 (17)
H4A—C4—H4B	108.1	N1—C15—H15A	108.8
C5—C4—H4A	109.6	N1—C15—H15B	108.8

C5—C4—H4B	109.6	C14—C15—H15A	108.8
N1—C5—C4	115.86 (17)	C14—C15—H15B	108.8
N1—C5—H5A	108.3	H15A—C15—H15B	107.7
N1—C5—H5B	108.3	Cl3—C16—Cl4	111.88 (14)
C4—C5—H5A	108.3	Cl3—C16—H16A	109.2
C4—C5—H5B	108.3	Cl3—C16—H16B	109.2
H5A—C5—H5B	107.4	Cl4—C16—H16A	109.2
N1—C6—H6A	109.6	Cl4—C16—H16B	109.2
N1—C6—H6B	109.6	H16A—C16—H16B	107.9
Ni1—N1—C5—C4	−176.58 (14)	C5—N1—C6—C7	76.4 (2)
Ni1—N1—C6—C7	−44.96 (17)	C5—N1—C15—C14	−66.4 (2)
Ni1—N1—C15—C14	60.23 (18)	C6—N1—C5—C4	70.2 (2)
Ni1—N2—C7—C6	−38.32 (18)	C6—N1—C15—C14	171.07 (16)
Ni1—N2—C8—C9	56.7 (2)	C7—N2—C8—C9	−176.54 (17)
Ni1—N3—C10—C9	−55.8 (2)	C8—N2—C7—C6	−170.52 (16)
Ni1—N3—C11—C12	40.53 (18)	C8—C9—C10—N3	69.4 (2)
Ni1—N4—C12—C11	38.96 (18)	C10—N3—C11—C12	170.10 (16)
Ni1—N4—C13—C14	−56.4 (2)	C11—N3—C10—C9	−179.93 (17)
N1—C6—C7—N2	59.0 (2)	C12—N4—C13—C14	−178.54 (17)
N2—C8—C9—C10	−69.0 (2)	C13—N4—C12—C11	165.79 (17)
N3—C11—C12—N4	−54.8 (2)	C13—C14—C15—N1	−75.3 (2)
N4—C13—C14—C15	70.1 (2)	C15—N1—C5—C4	−52.9 (2)
C2—C3—C4—C5	177.92 (18)	C15—N1—C6—C7	−160.86 (16)
C3—C4—C5—N1	−164.91 (18)		

Table 4. Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.01128 (14)	0.01211 (14)	0.01082 (14)	0.00405 (10)	0.00308 (10)	0.00461 (10)
Cl1	0.0144 (2)	0.0149 (3)	0.0123 (2)	0.0038 (2)	0.00155 (19)	0.0036 (2)
O1	0.0166 (8)	0.0162 (8)	0.0120 (8)	0.0062 (7)	0.0021 (6)	0.0042 (6)
N1	0.0134 (8)	0.0144 (9)	0.0120 (8)	0.0047 (7)	0.0031 (7)	0.0049 (7)
N2	0.0138 (9)	0.0138 (9)	0.0125 (8)	0.0042 (7)	0.0038 (7)	0.0041 (7)
N3	0.0137 (9)	0.0161 (9)	0.0128 (8)	0.0053 (7)	0.0031 (7)	0.0052 (7)
N4	0.0129 (8)	0.0151 (9)	0.0128 (8)	0.0054 (7)	0.0034 (7)	0.0043 (7)
C1	0.0290 (13)	0.0191 (12)	0.0160 (11)	0.0054 (10)	0.0051 (10)	0.0047 (9)
C2	0.0252 (12)	0.0166 (12)	0.0141 (11)	0.0083 (10)	0.0019 (9)	0.0044 (9)
C3	0.0205 (11)	0.0173 (11)	0.0141 (10)	0.0080 (9)	0.0044 (9)	0.0055 (9)

C4	0.0170 (11)	0.0212 (12)	0.0150 (10)	0.0054 (9)	0.0049 (9)	0.0066 (9)
C5	0.0156 (10)	0.0149 (11)	0.0126 (10)	0.0037 (9)	0.0033 (8)	0.0028 (8)
C6	0.0175 (11)	0.0135 (11)	0.0145 (10)	0.0035 (9)	0.0048 (8)	0.0062 (8)
C7	0.0187 (11)	0.0161 (11)	0.0157 (10)	0.0071 (9)	0.0045 (9)	0.0072 (9)
C8	0.0132 (10)	0.0172 (11)	0.0187 (11)	0.0077 (9)	0.0039 (8)	0.0052 (9)
C9	0.0146 (10)	0.0204 (12)	0.0159 (11)	0.0073 (9)	0.0058 (8)	0.0042 (9)
C10	0.0145 (10)	0.0197 (12)	0.0179 (11)	0.0048 (9)	0.0070 (9)	0.0068 (9)
C11	0.0181 (11)	0.0172 (11)	0.0176 (11)	0.0054 (9)	0.0061 (9)	0.0091 (9)
C12	0.0183 (11)	0.0158 (11)	0.0179 (11)	0.0071 (9)	0.0054 (9)	0.0093 (9)
C13	0.0135 (10)	0.0182 (11)	0.0172 (11)	0.0070 (9)	0.0036 (8)	0.0050 (9)
C14	0.0139 (10)	0.0213 (12)	0.0154 (10)	0.0079 (9)	0.0048 (8)	0.0047 (9)
C15	0.0122 (10)	0.0212 (12)	0.0148 (10)	0.0053 (9)	0.0045 (8)	0.0079 (9)
Cl2	0.0174 (3)	0.0187 (3)	0.0151 (2)	0.0068 (2)	0.0019 (2)	0.0043 (2)
Cl3	0.0405 (4)	0.0369 (4)	0.0386 (4)	0.0048 (3)	0.0173 (3)	0.0048 (3)
Cl4	0.0681 (5)	0.0436 (4)	0.0299 (4)	0.0222 (4)	0.0183 (3)	0.0134 (3)
C16	0.0369 (15)	0.0436 (17)	0.0295 (14)	0.0223 (13)	0.0141 (12)	0.0186 (12)

Table 5. Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*A*···Cl2	0.83 (2)	2.28 (2)	3.0987 (16)	173 (2)
O1—H1*B*···Cl2^{i}	0.81 (2)	2.35 (2)	3.1584 (16)	173 (2)

[Ni(hexynyl-cyclam)]$^{2+}$

Experimental Summary

The single crystal X-ray diffraction studies were carried out on a Bruker Kappa APEX-II CCD diffractometer equipped with Cu K_α radiation (λ = 1.5478). A 0.217 x 0.053 x 0.041 mm piece of a light purple needle was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using ϕ and ϖ scans. Crystal-to-detector distance was 40 mm using variable exposure time (10s-20s) depending on θ with a scan width of 1.0°. Data collection was 99.2% complete to 68.00° in θ. A total of 16660 reflections were collected covering the indices, -10<=h<=10, -11<=k<=10, -14<=l<=16. 3812 reflections were found to be symmetry independent, with a R_{int} of 0.0551. Indexing and unit cell refinement indicated a primitive, monoclinic lattice. The space group was found to be $P2_1/n$. The data were integrated using the Bruker SAINT software program and scaled using the SADABS software program. Solution by direct methods (SHELXT) produced a complete phasing model consistent with the proposed structure.

All nonhydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014. Crystallographic data are summarized in Table 1.

Table 1. Crystal data and structure refinement for AZ164.

Report date	2017-09-07	
Identification code	AZ188	
Empirical formula	C16 H34 Cl N4 Ni O, Cl	
Molecular formula	C16 H34 Cl2 N4 Ni O	
Formula weight	428.08	
Temperature	100.0 K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.5522 (3) Å	□= 109.220 (2)°
	b = 9.3730 (3) Å	□= 99.489 (2)°
	c = 13.4983 (4) Å	□ = 91.607 (2)°
Volume	1003.79 (6) $Å^3$	
Z	2	
Density (calculated)	1.469 Mg/m^3	
Absorption coefficient	1.244 mm^{-1}	
F(000)	456	
Crystal size	0.1 x 0.05 x 0.05 mm^3	
Crystal color, habit	Light Purple Needle	
Theta range for data collection	2.310 to 25.682°.	
Index ranges	-10<=h<=10, -11<=k<=10, -14<=l<=16	
Reflections collected	16660	
Independent reflections	3812 [R(int) = 0.0551, R(sigma) = 0.0529]	
Completeness to theta = 68.000°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0. 0.4908 and 0.4457	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3812 / 2 / 223	
Goodness-of-fit on F^2	1.026	
Final R indices [I>2sigma(I)]	R1 = 0.0388, wR2 = 0.0833	
R indices (all data)	R1 = 0.0621, wR2 = 0.0924	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.583 and -0.331 $e.Å^{-3}$	

Table 2. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Ni1	0.43848 (4)	0.68977 (4)	0.78460 (3)	0.01231 (12)
Cl1	0.33968 (9)	0.80839 (8)	0.95673 (6)	0.01887 (19)
O1	0.5490 (3)	0.5688 (2)	0.65130 (17)	0.0177 (5)
N1	0.2843 (3)	0.7997 (3)	0.69710 (18)	0.0139 (5)
N2	0.2844 (3)	0.4981 (3)	0.74834 (19)	0.0167 (6)
N3	0.5907 (3)	0.5879 (3)	0.87341 (19)	0.0162 (6)
N4	0.5915 (3)	0.8813 (3)	0.82941 (19)	0.0153 (6)
C1	0.0968 (4)	0.7546 (4)	0.1332 (3)	0.0285 (8)
C2	0.0906 (4)	0.8062 (3)	0.2260 (3)	0.0216 (7)
C3	0.0919 (4)	0.8623 (4)	0.3396 (3)	0.0243 (8)
C4	0.2089 (4)	0.7883 (4)	0.4036 (2)	0.0223 (7)
C5	0.1738 (4)	0.8241 (4)	0.5157 (2)	0.0242 (8)
C6	0.2884 (4)	0.7515 (4)	0.5806 (2)	0.0196 (7)
C7	0.1188 (4)	0.7790 (3)	0.7144 (2)	0.0183 (7)
C8	0.0528 (4)	0.6123 (3)	0.6766 (2)	0.0200 (7)
C9	0.1156 (4)	0.5257 (4)	0.7501 (3)	0.0206 (7)
C10	0.3478 (4)	0.4185 (3)	0.8234 (2)	0.0188 (7)
C11	0.5279 (4)	0.4271 (3)	0.8379 (2)	0.0184 (7)
C12	0.7635 (4)	0.6103 (3)	0.8756 (3)	0.0201 (7)
C13	0.8223 (4)	0.7770 (3)	0.9101 (2)	0.0203 (7)
C14	0.7620 (4)	0.8601 (3)	0.8335 (2)	0.0194 (7)
C15	0.5303 (4)	0.9740 (3)	0.7637 (2)	0.0184 (7)
C16	0.3497 (4)	0.9614 (3)	0.7495 (2)	0.0175 (7)
Cl2	0.69346 (9)	0.70881 (9)	0.50121 (6)	0.0233 (2)

Table 3. Geometric parameters. Bond lengths [Å] and angles [°]

Ni1—Cl1	2.5194 (8)	C5—H5B	0.9900
Ni1—O1	2.166 (2)	C5—C6	1.529 (4)
Ni1—N1	2.135 (2)	C6—H6A	0.9900
Ni1—N2	2.068 (2)	C6—H6B	0.9900
Ni1—N3	2.086 (2)	C7—H7A	0.9900
Ni1—N4	2.048 (2)	C7—H7B	0.9900
O1—H1A	0.826 (18)	C7—C8	1.533 (4)
O1—H1B	0.818 (18)	C8—H8A	0.9900
N1—C6	1.493 (4)	C8—H8B	0.9900
N1—C7	1.489 (4)	C8—C9	1.520 (4)
N1—C16	1.492 (4)	C9—H9A	0.9900
N2—H2	1.0000	C9—H9B	0.9900
N2—C9	1.477 (4)	C10—H10A	0.9900
N2—C10	1.490 (4)	C10—H10B	0.9900
N3—H3	1.0000	C10—C11	1.517 (4)
N3—C11	1.478 (4)	C11—H11A	0.9900
N3—C12	1.481 (4)	C11—H11B	0.9900
N4—H4	1.0000	C12—H12A	0.9900
N4—C14	1.471 (4)	C12—H12B	0.9900
N4—C15	1.482 (4)	C12—C13	1.520 (4)
C1—H1	0.9500	C13—H13A	0.9900
C1—C2	1.196 (4)	C13—H13B	0.9900
C2—C3	1.445 (4)	C13—C14	1.523 (4)
C3—H3A	0.9900	C14—H14A	0.9900
C3—H3B	0.9900	C14—H14B	0.9900
C3—C4	1.542 (4)	C15—H15A	0.9900
C4—H4A	0.9900	C15—H15B	0.9900
C4—H4B	0.9900	C15—C16	1.521 (4)
C4—C5	1.522 (4)	C16—H16A	0.9900
C5—H5A	0.9900	C16—H16B	0.9900
O1—Ni1—Cl1	170.46 (6)	N1—C6—H6B	108.3
N1—Ni1—Cl1	94.63 (6)	C5—C6—H6A	108.3
N1—Ni1—O1	94.91 (8)	C5—C6—H6B	108.3
N2—Ni1—Cl1	90.36 (7)	H6A—C6—H6B	107.4
N2—Ni1—O1	88.52 (9)	N1—C7—H7A	108.9
N2—Ni1—N1	95.96 (10)	N1—C7—H7B	108.9

N2—Ni1—N3	85.16 (10)	N1—C7—C8	113.4 (2)
N3—Ni1—Cl1	84.32 (7)	H7A—C7—H7B	107.7
N3—Ni1—O1	86.15 (9)	C8—C7—H7A	108.9
N3—Ni1—N1	178.47 (10)	C8—C7—H7B	108.9
N4—Ni1—Cl1	86.83 (7)	C7—C8—H8A	108.5
N4—Ni1—O1	93.99 (9)	C7—C8—H8B	108.5
N4—Ni1—N1	85.86 (9)	H8A—C8—H8B	107.5
N4—Ni1—N2	176.78 (10)	C9—C8—C7	114.9 (3)
N4—Ni1—N3	92.98 (10)	C9—C8—H8A	108.5
Ni1—O1—H1A	113 (2)	C9—C8—H8B	108.5
Ni1—O1—H1B	129 (2)	N2—C9—C8	112.1 (2)
H1A—O1—H1B	104 (3)	N2—C9—H9A	109.2
C6—N1—Ni1	115.05 (17)	N2—C9—H9B	109.2
C7—N1—Ni1	109.19 (17)	C8—C9—H9A	109.2
C7—N1—C6	110.6 (2)	C8—C9—H9B	109.2
C7—N1—C16	110.7 (2)	H9A—C9—H9B	107.9
C16—N1—Ni1	101.60 (17)	N2—C10—H10A	109.8
C16—N1—C6	109.4 (2)	N2—C10—H10B	109.8
Ni1—N2—H2	107.5	N2—C10—C11	109.4 (2)
C9—N2—Ni1	115.36 (18)	H10A—C10—H10B	108.2
C9—N2—H2	107.5	C11—C10—H10A	109.8
C9—N2—C10	112.1 (2)	C11—C10—H10B	109.8
C10—N2—Ni1	106.48 (18)	N3—C11—C10	108.9 (2)
C10—N2—H2	107.5	N3—C11—H11A	109.9
Ni1—N3—H3	106.2	N3—C11—H11B	109.9
C11—N3—Ni1	106.20 (18)	C10—C11—H11A	109.9
C11—N3—H3	106.2	C10—C11—H11B	109.9
C11—N3—C12	114.0 (2)	H11A—C11—H11B	108.3
C12—N3—Ni1	117.34 (18)	N3—C12—H12A	109.1
C12—N3—H3	106.2	N3—C12—H12B	109.1
Ni1—N4—H4	105.8	N3—C12—C13	112.3 (2)
C14—N4—Ni1	117.03 (18)	H12A—C12—H12B	107.9
C14—N4—H4	105.8	C13—C12—H12A	109.1
C14—N4—C15	113.8 (2)	C13—C12—H12B	109.1
C15—N4—Ni1	107.78 (18)	C12—C13—H13A	108.2
C15—N4—H4	105.8	C12—C13—H13B	108.2
C2—C1—H1	180.0	C12—C13—C14	116.3 (3)

C1—C2—C3	176.0 (3)	H13A—C13—H13B	107.4
C2—C3—H3A	108.8	C14—C13—H13A	108.2
C2—C3—H3B	108.8	C14—C13—H13B	108.2
C2—C3—C4	113.9 (3)	N4—C14—C13	111.6 (2)
H3A—C3—H3B	107.7	N4—C14—H14A	109.3
C4—C3—H3A	108.8	N4—C14—H14B	109.3
C4—C3—H3B	108.8	C13—C14—H14A	109.3
C3—C4—H4A	109.7	C13—C14—H14B	109.3
C3—C4—H4B	109.7	H14A—C14—H14B	108.0
H4A—C4—H4B	108.2	N4—C15—H15A	110.1
C5—C4—C3	110.0 (3)	N4—C15—H15B	110.1
C5—C4—H4A	109.7	N4—C15—C16	107.8 (2)
C5—C4—H4B	109.7	H15A—C15—H15B	108.5
C4—C5—H5A	109.5	C16—C15—H15A	110.1
C4—C5—H5B	109.5	C16—C15—H15B	110.1
C4—C5—C6	110.9 (3)	N1—C16—C15	110.4 (2)
H5A—C5—H5B	108.1	N1—C16—H16A	109.6
C6—C5—H5A	109.5	N1—C16—H16B	109.6
C6—C5—H5B	109.5	C15—C16—H16A	109.6
N1—C6—C5	115.8 (2)	C15—C16—H16B	109.6
N1—C6—H6A	108.3	H16A—C16—H16B	108.1

Table 4. Atomic displacement parameters (A^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.0150 (2)	0.0115 (2)	0.0108 (2)	0.00262 (15)	0.00466 (15)	0.00318 (15)
Cl1	0.0247 (4)	0.0177 (4)	0.0132 (4)	0.0022 (3)	0.0090 (3)	0.0012 (3)
O1	0.0231 (13)	0.0171 (12)	0.0129 (12)	0.0023 (10)	0.0073 (10)	0.0031 (9)
N1	0.0154 (13)	0.0141 (13)	0.0116 (13)	0.0036 (10)	0.0052 (11)	0.0022 (10)
N2	0.0194 (14)	0.0159 (14)	0.0150 (14)	0.0012 (11)	0.0045 (11)	0.0047 (11)
N3	0.0189 (14)	0.0159 (14)	0.0144 (13)	0.0023 (11)	0.0046 (11)	0.0051 (11)
N4	0.0192 (14)	0.0145 (14)	0.0125 (13)	0.0017 (11)	0.0050 (11)	0.0042 (11)
C1	0.032 (2)	0.033 (2)	0.026 (2)	0.0040 (16)	0.0061 (16)	0.0155 (16)
C2	0.0206 (18)	0.0195 (18)	0.029 (2)	−0.0016 (14)	−0.0002 (15)	0.0169 (15)
C3	0.0280 (19)	0.0181 (18)	0.0283 (19)	0.0065 (14)	0.0073 (15)	0.0084 (15)
C4	0.0283 (19)	0.0222 (18)	0.0189 (17)	0.0076 (15)	0.0071 (15)	0.0084 (14)
C5	0.0261 (19)	0.0272 (19)	0.0205 (18)	0.0103 (15)	0.0066 (15)	0.0078 (15)
C6	0.0188 (17)	0.0216 (18)	0.0189 (17)	0.0046 (14)	0.0068 (14)	0.0055 (14)

C7	0.0160 (16)	0.0201 (17)	0.0212 (17)	0.0058 (13)	0.0073 (13)	0.0079 (14)
C8	0.0127 (16)	0.0259 (19)	0.0218 (17)	0.0026 (14)	0.0036 (14)	0.0084 (14)
C9	0.0182 (17)	0.0207 (18)	0.0229 (18)	−0.0020 (14)	0.0072 (14)	0.0059 (14)
C10	0.0224 (17)	0.0142 (16)	0.0206 (17)	0.0018 (13)	0.0051 (14)	0.0064 (13)
C11	0.0244 (18)	0.0130 (16)	0.0191 (17)	0.0040 (13)	0.0037 (14)	0.0071 (13)
C12	0.0174 (17)	0.0222 (18)	0.0229 (18)	0.0057 (13)	0.0034 (14)	0.0104 (14)
C13	0.0176 (17)	0.0231 (18)	0.0212 (17)	0.0024 (14)	0.0057 (14)	0.0077 (14)
C14	0.0181 (17)	0.0185 (17)	0.0208 (17)	0.0006 (13)	0.0076 (14)	0.0037 (14)
C15	0.0239 (18)	0.0119 (16)	0.0180 (16)	0.0002 (13)	0.0042 (14)	0.0032 (13)
C16	0.0262 (18)	0.0115 (16)	0.0163 (16)	0.0066 (13)	0.0047 (14)	0.0059 (13)
Cl2	0.0253 (4)	0.0233 (4)	0.0190 (4)	−0.0008 (3)	0.0083 (3)	0.0023 (3)

12.Authors contribution.

All authors contributed to this manuscript equally.

13. References

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