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# Synthesis of new metal-free 1,2,4,5,9,10,12,13-octaaza[16] annulene derivatives using the reaction of vinamidinium salts with thiocarbohydrazide

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**Abstract**

A new series of marcocyclic ligands, 1,2,4,5,9,10,12,13-octaaza[16]annulene derivatives were synthesized by using the condensation reaction of the correspondingly [2+2] 2-heteroaryl-substituted vinamidinium salts or phenyl vinamidinium salts and derivatives or halo-substituted vinamidinum salt [1A-10A] with thiocarbohydrazide in ethanolic medium under mild condition. Metal complexes were formed by reacting of ethanolic solution of Co, Ni, and Zn with macrocyclic ligand in ethanolic medium under mild condition. Purposed complexes have been characterized with the help of elemental analyses, comparative absorption band of $\nu$(C=N), mass, and NMR. Geometry and complex formulation are out of scope of this work. The biological activities of carohydrazide and thiocarbohydrazide base of the ligands and purposed complexes such as antimicrobial, antitumor, and insecticides have attracted significant attention in bioorganic chemistry.

**KEYWORDS**

marcocyclic complexes, marcocyclic ligands, thiocarbohydrazid, Vilsmier–Haack reaction conditions, vinamidinium salt

## 1 | INTRODUCTION

Substituted functional macrocycles play an important role in supramolecular chemistry.[1,2] The chemistry of heteromacrocyclic compounds has been investigated in recent years on account of its various applications in bioinorganic chemistry and biological processes.[3] Transition metal complexes have been applied in wide variety fields such as antifungal, analgesic, sedative, antipyretic, and anti-inflammatory agents.[4–8] Synthesis of heteromacrocyclic compounds via vinamidinium salts is easy and suitable method.[9–11] Vinamidinium salts are prepared under Vilsmeier–Haack conditions from aryl acetic acids and undergo condensation reaction to produce heteromacrocyclic ligands.[12] Heteromacrocyclic complexes contain a Hückel anti-aromatic 4n $\pi$-system within the 16-membered inner ring are antiaromatic and their central cavity is smaller than in porphyrins and, as a consequence, the metal-nitrogen distance is shorter and the complexes are more stable.[13] Some macrocycles containing heteroatoms and functional groups have been investigated as functional molecules.[14] Ring size and metal ion are key function in macrocycles.[15] A novel Schiff base decaaza complex synthesized by Shakir et al.[16] A number of octa-aza annulene are synthesized and studied. The synthesis of 14-membered octaaza macrocycle benzyl bis(hydrazone) with aldehyde has been reported.[17] Hydrazones are used for the synthesis of heterocycles, drug design, and as ligands for metal complexes, antimicrobial, antitumor, and insecticides.[18–21] The condensation reactions of [2+2] carbohydrazide or thiocarbohydrazide with 3,4-hexanedione are used for synthesis of octaaza macrocyclic Schiff base.[22,23] Medicinal applications of carbohydrazide and thiocarbohydrazide are important reason for synthesize and characterize such macrocyclic complexes.[24] In this work, we report the synthesis and characterization of 16-membered octaaza macrocyclic ligands obtained via the condensation reaction between thiocarbohydrazide (TCH) and vinamidinium salts in ethanolic solvent under mild condition. In continuation of our research on the applications of macrocyclic ligands, we report herein a simple method for the synthesis of three macrocyclic complexes via the condensation reaction between 16-membered octaaza macrocyclic ligand and transition metals Co, Ni, and Zn in ethanolic solvent under mild condition.

## 2 | RESULTS AND DISCUSSION

### 2.1 | IR spectra

The IR information about the thiocarbohydrazide (TCH) was showed the pair bands of $NH_2$ in $\nu$ (3275, 3307), but these bands were disappeared in spectrum of the free ligands.[25,26] Characteristic IR bands ($cm^{-1}$) of the ligand and complex were showed in Table 1. The appearance of N–H stretch single band in $\nu$(3,250–3650) and imine group (C=N) formation in $\nu$(1607) indicate the formation of macrocyclic ligand.[27,28] The $\nu$(C=N) shifting to the lower value in the complex showed a drift of lone pair density of azomethine nitrogen toward the metal atom and was coordinated with metal.[29] Appearance of $\nu$(653–685) indicates coordination of (M-N).[30]

### 2.2 | NMR

In the $^{13}$C-NMR spectrum of the TCH, a signal was appeared at 180 ppm due to C=S, but this signal in the ligand was shifted to 138 ppm, in addition a signal in the $^{1}$H-NMR spectrum of ligand in 3.4 ppm(s, H) was attributed to C-SH. In TCH $^{1}$H-NMR spectrum, $NH_2$ was appeared in 4.48 ppm and NH 7.98 ppm but this signals was absent in ligand. Signals at 10.8–10.9 ppm(d,2H) and signal at 12.98 ppm(broad,2H) in the ligand spectrum can be assigned to NH. Benzo-H was appeared in 7.408–7.785 ppm(m,8H). The HC=C $^{1}$H-NMR spectrum signals were appeared in 8.1 ppm(s,2H) and 8.8 ppm (s,2H) and $^{13}$C-NMR at 167.2 and 151.4 ppm (Figure 1). Phenyl vinamidinum salt as a first material $^{1}$H-NMR HC=C appeared in 7.7 ppm(s,2H) and $^{13}$C-NMR at 163.38 because of conjugation. According to these evidences including SH group, two NH groups, two phenyl groups, two groups of HC=C and absent of NH2, indicate formation of macrocyclic ligand [1B-10B].

**TABLE 1** Table characteristic IR bands ($cm^{-1}$) of the ligand and complex

| Entry | $\nu$(C=N) | $\nu$(NH) | $\nu$(M-N) |
|---|---|---|---|
| Ligand | 1582 | 3430 | |
| Co-Ligand | 1425 | 3390 | 683 |
| Ni-Ligand | 1448 | 3392 | 673 |
| Zn-Ligand | 1504 | 3397 | 685 |

Purposed mechanism for the synthesis of 7,15-bis(R)-1,2,4,5,9,10,12,13-octaazacyclohexadeca-2,5,7,10,13,15-hexaene-3,11-dithiol(B) (Scheme 1), by using the condensation reaction of the correspondingly [2+2] 2-heteroaryl-substituted vinamidinium salts or phenyl and derivatives vinamidinium salts or halo-substituted vinamidinum salt [1A-10A] with thiocarbohydrazide in ethanolic medium under mild condition. Vinamidinium salt was attacked by amine group of TCH in presence of i-$Pr_2$NEt and then elimination of dimethylamine was occurred (Scheme 2). Product (B) was obtained by an intramolecular nucleophilic cyclization on the iminium salt[31] (Scheme 2).

The effect of reagent, solvent, temperature, and time is illustrated in Table 2. i-$Pr_2$NEt in EtOH at 50°C proved to be the best (Table 2, entry 8).

Metal complexes were prepared by reaction of ligands [**1B-10B**] with metals [Co, Ni, and Zn] in ethanolic solution under mild condition (Scheme 3). Proposed geometry was suggested as octahedral.[32] Geometry and complex formulation are out of scope of this work.

## 3 | CONCLUSION

Our study shows the feasibility of synthesizing 16-membered octaaza macrocyclic ligands. The thiocarbohydrazide acted as bidentate ligand. The condensation of vnamidinium salts with thiocarbohydrazide leads to the synthesis of 16-membered annulene. The formation of the macrocyclic ligand was confirmed by FT-IR, NMR, and mass. The macrocyclic Schiff base ligand acts as a tetradentate is coordinated through the four nitrogen atoms with the metal ion to form complex.

## 4 | EXPERIMENTAL SECTION

### 4.1 | General information

*Materials and measurements*: Chemicals were purchased from Merck and Sigmaaldrich. Vinamidinium salts

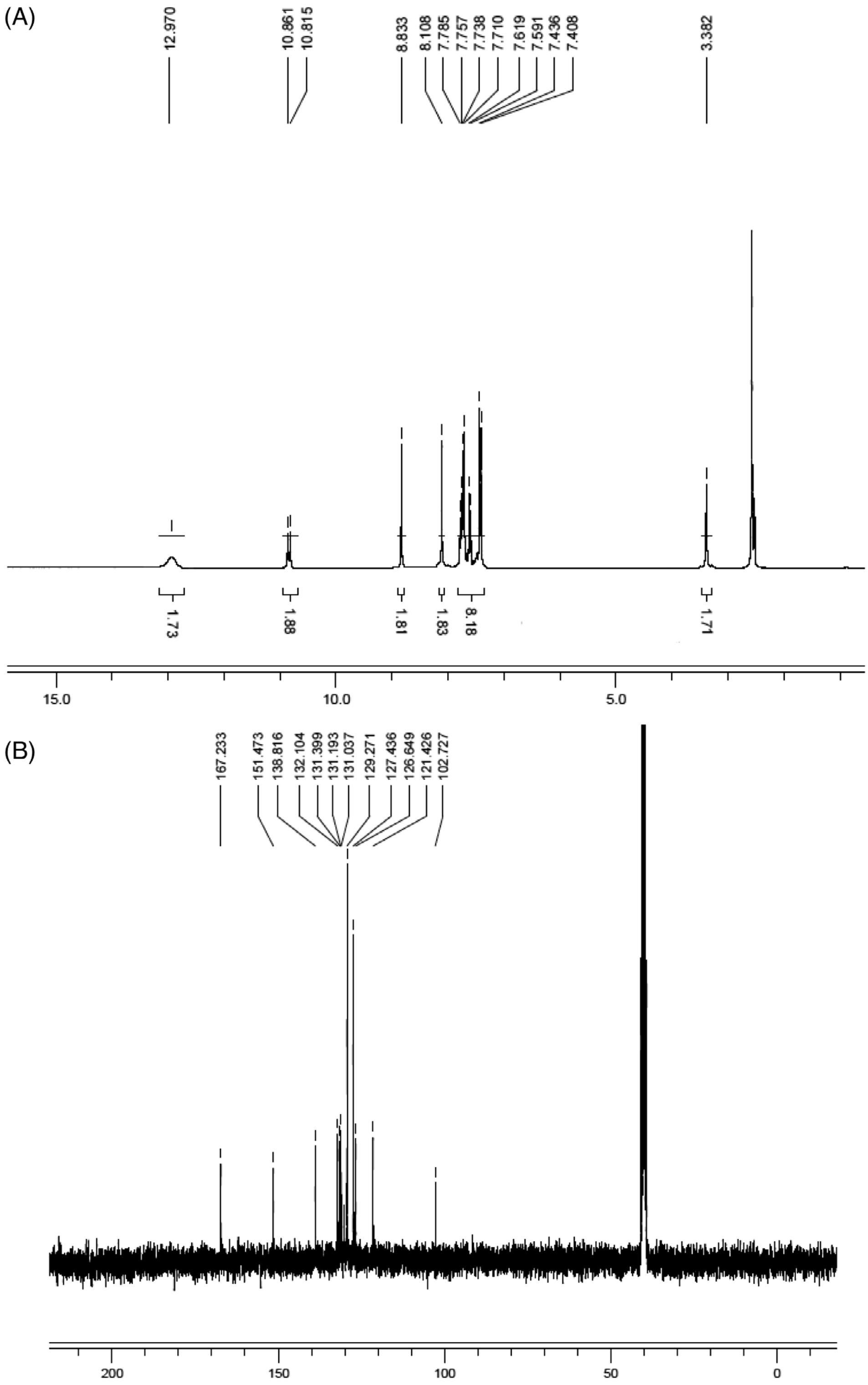
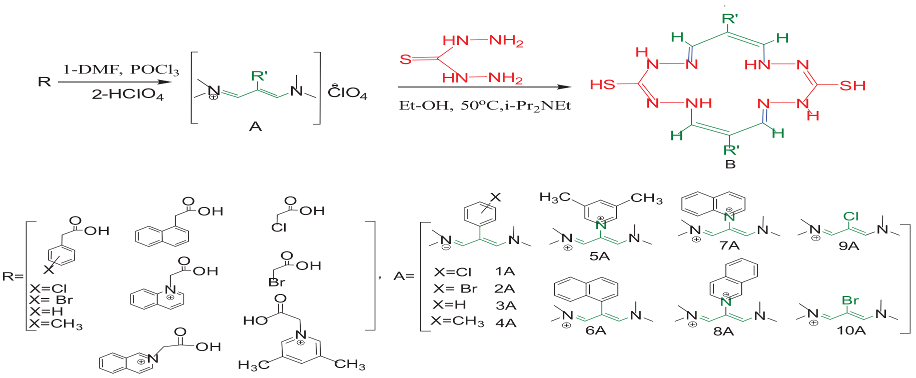
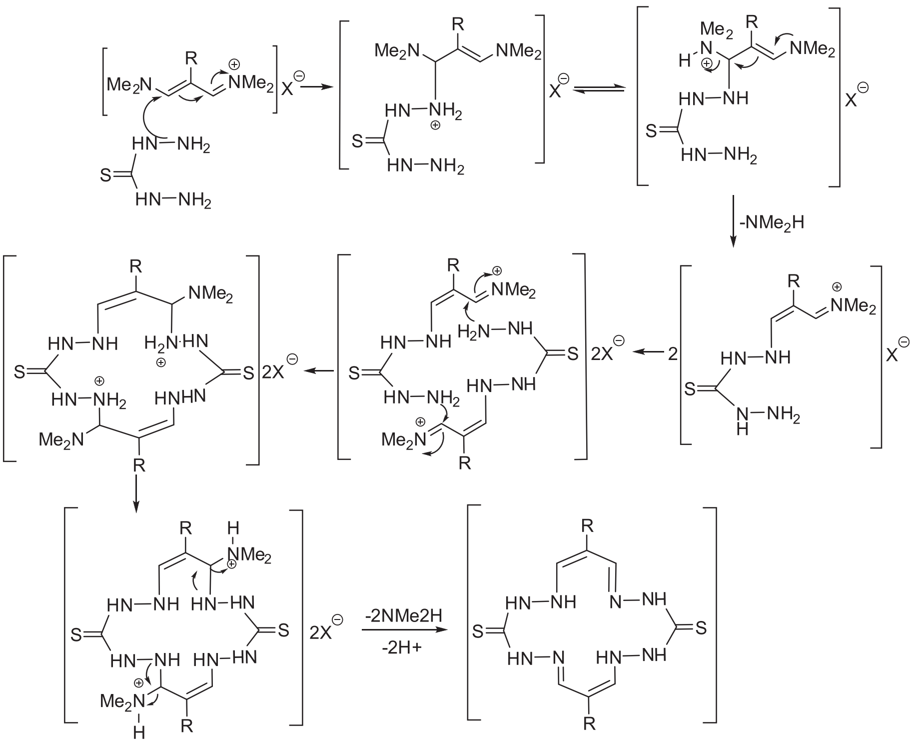


**FIGURE 1** (A) $^1$H.NMR, (B) $^{13}$C. NMR of 7,15-bis(4-chlorophenyl)-1,2,4,5,9,10,12,13-octaazacyclohexadeca-2,5,7,10,13,15-hexaene-3,11-dithiol (1B)

[1A-10A] were prepared according to literature procedures.[33–36] Thiocarbohydrazide was synthesized according to literature procedures.[37,38] 1H and 13C-NMR spectra were recorded with a Bruker Avance DRX-300. d6-DMSO was used as solvent and TMS as internal standard. Mass spectral data were obtained on a Finnigan-Matt 8430 (70-eV) spectrometer. The IR spectra were obtained with a Perkin-Elmer 781 spectrophotometer. Elemental analyses were made with a CHN Analyzer (Flash, 1112 series EA, Thermo Finnigan Company) and Electrothermal 9200 (Germany) was used for determination of melting points.



**SCHEME 1** Vinamidinium salts synthesis via Vilsmier-Haack reaction conditions (A) and condensation reaction with TCH lead to product (B) [Colour figure can be viewed at wileyonlinelibrary.com]

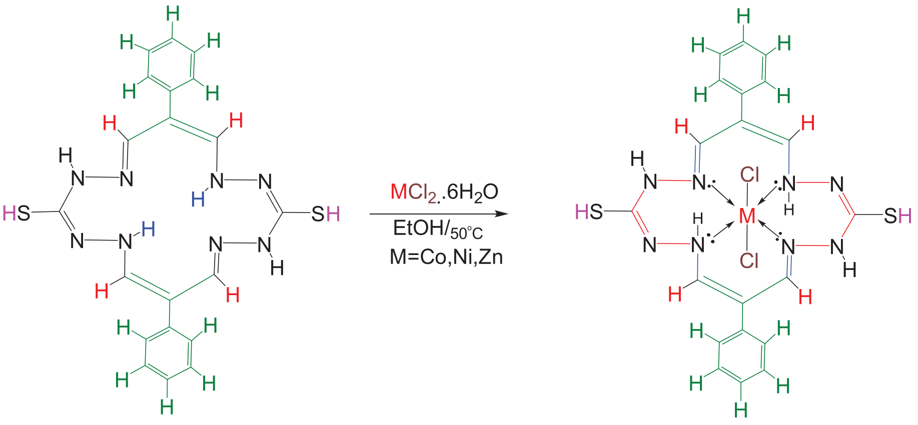


**SCHEME 2** Purposed mechanism for the synthesis of 7,15-bis(phenyl)-1,2,4,5,9,10,12,13-octaazacyclohexadeca-2,5,7,10,13,15-hexaene-3,11-dithiol and derivatives [1B-10B]

**TABLE 2** Effects of reagent and solvent on the reaction of 2-substituted vinamidinium salts with thiocarbohydrazid under different conditions

| Entry | Solvent | Reagent | Temp(°C) | Time (h) | Yield (%)[a] |
|---|---|---|---|---|---|
| 1 | EtOH | AcOH 5 drops | reflux | 24 | - |
| 2 | MeOH | AcOH 5 drops | reflux | 24 | - |
| 3 | $CH_3CN$ | AcOH 5 drops | reflux | 24 | - |
| 4 | $CH_2Cl_2$ | AcOH 5 drops | reflux | 24 | - |
| 5 | DMF | AcOH 5 drops | reflux | 24 | - |
| 6 | $CH_3CN$ | $i\text{-}Pr_2Net$ 5 drops | reflux | 7 | 50 |
| 7 | MeOH | $i\text{-}Pr_2NEt$ 5 drops | 50 | 15 | 58 |
| 8 | EtOH | $i\text{-}Pr_2NEt$ 5 drops | 50 | 3 | 63 |
| 9 | EtOH | $i\text{-}Pr_2Net$ 10 drops | 50 | 3 | 63 |
| 10 | EtOH | $i\text{-}Pr_2NEt$ 5 drops | 50 | 15 | 65 |
| 11 | EtOH | $i\text{-}Pr_2NEt$ 5 drops | 60 | 20 | 67 |

[a] Isolated yields.



3B

3C

**SCHEME 3** The purposed structure of the complex [M(L)Cl$_2$], M = Co, Ni, Zn [Colour figure can be viewed at wileyonlinelibrary.com]

### 4.1.1 | General procedure for the synthesis of ligand of 7,15-bis(phenyl)-1,2,4,5,9,10,12,13-octaazacyclohexadeca-2,5,7,10,13,15-hexaene-3,11-dithiol

Thiocarbohydrazide 1.0 mmol was added in 7.0 mL of ethanol in a round-bottom flask. The solution was heated up to 50°C and then 1.0 mmol vinamidinium salt and 5 drops of i-Pr$_2$NEt were added. The reaction mixture was refluxed at 50°C for 3 hours. After the formation of red precipitate, Distilled water 50 mL was added and heated at 50°C for 30 minutes. The red precipitate was collected by filtration, washed with warm water and dried. The residue was washed with 7 mL warm ethyl acetate, warm distilled water, and dried under vacuum at 50°C (Table 3).

### 4.1.2 | General procedure for the synthesis of complex of 7,15-bis(phenyl)-1,2,4,5,9,10,12,13-octaazacyclohexadeca-2,5,7,10,13,15-hexaene-3,11-dithiol

Ligand (L) (436 mg, 1 mmol.) was added to 25 mL ethanol and heated up to 50°C. Hot ethanolic solution (10 mL) of CoCl$_2$.6H2O (237 mg, 1 mmol) or NiCl$_2$.6H2O (237 mg, 1 mmol) or ZnCl2 (136 mg, 1 mmol.) was added to ligand solution with constant stirring. The mixture was refluxed for (5) hours at 50°C. A precipitate was formed. It was filtered, washed several times with EtOH, and then washed with diethyl ether and dried under vacuum at 50°C.

### 4.1.3 | 7,15-bis(4-chlorophenyl)-1,2,4,5,9,10,12,13-octaazacyclohexadeca-2,5,7,10,13,15-hexaene-3,11-dithiol (1B)

Red powder; m.p. 198–200°C; Yield 65%;UV–Vis: 337, 387 nm; IR(KBr): ύ = 3250–3650 (broad) cm$^{-1}$ (NH), 1585 (s) cm$^{-1}$(C=N), $^1$H-NMR (d6-DMSO) δ /ppm: 3.382 (s,2H,SH), 7.408–7.785 (m,8H, benzo-H), 8.108(s,2H, HC=C), 8.833(s,2H, HC=C), 10.815–10. 861 (d,J = 13.8.2 Hz, 2H,NH), 12.970 (broad,2H,NH). $^{13}$C-NMR (d6-DMSO) δ /ppm: 102.727, 121.426, 126.649, 127.436, 129.271, 131.037, 131.193, 131.399, 132.104, 138.816, 151.473, 167.233, Mass spectrum: m/e = 505, Anal. calcd for ($C_{20}H_{18}N_8S_2Cl_2$): C, 47.52; H, 3.56; N, 22.18. Found: C, 47.78; H, 3.49; N, 21.97.

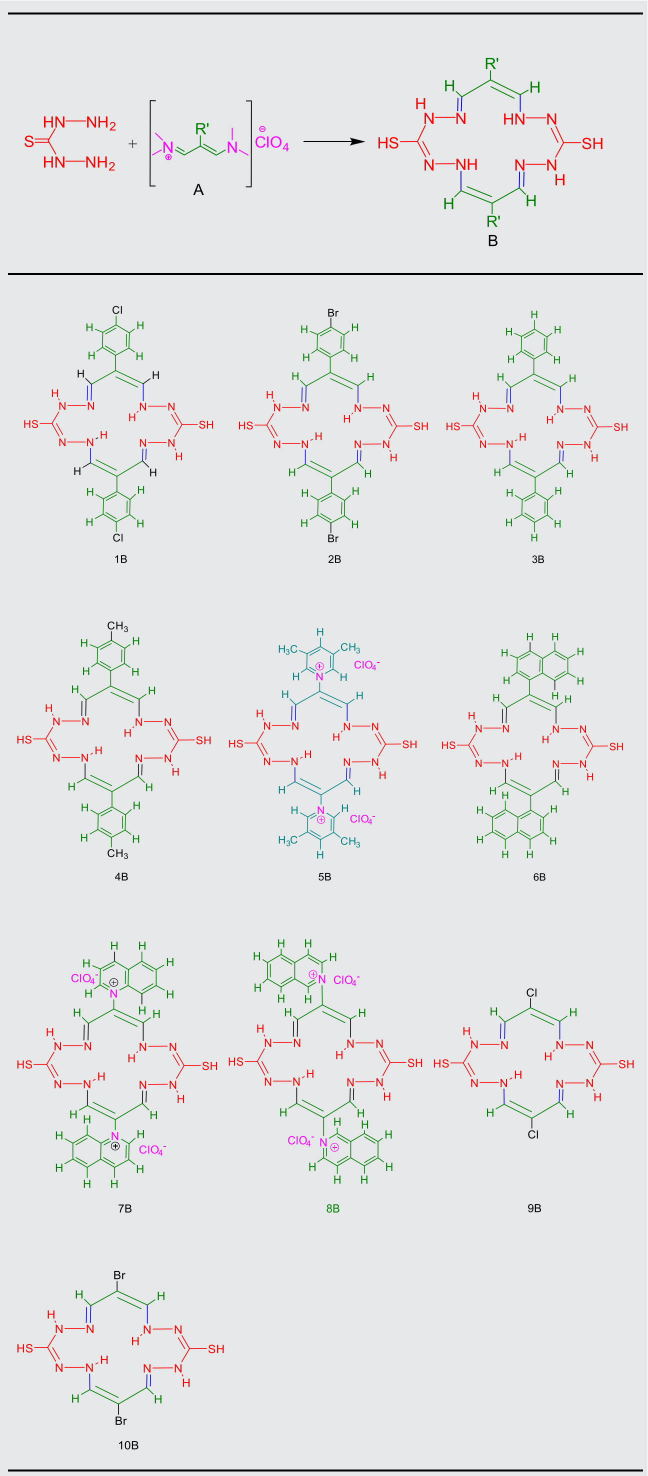
### 4.1.4 | 7,15-bis(4-bromoophenyl)-1,2,4,5,9,10,12,13-octaazacyclohexadeca-2,5,7,10,13,15-hexaene-3,11-dithiol (2B)

Red powder; m.p. 198–200°C; Yield 68%; %; UV–Vis: 292, 453 nm; IR(KBr): ύ = 3250–3650 (broad) cm$^{-1}$ (NH), 1584 (s) cm$^{-1}$(C=N), $^1$H-NMR (d6-DMSO): δ/ppm = 3.132(s,2H,SH), 7.557–7.586 (m,8H, benzo-H), 8.097 (s,2H,HC=C), 8.828(s,2H, HC=C), 10.810–10.855 (d,J = 13.5 Hz, 2H,NH),12.975 (broad,2H,NH). $^{13}$C-NMR (d6-DMSO): δ /ppm = 103.710, 119.844, 126.510, 127.782, 129.743, 130.944, 131.151, 131.560, 131.901, 140.777, 151.617, 167.810, Mass spectrum: m/e = 595, Anal. calcd for ($C_{20}H_{18}N_8S_2Br_2$): C, 40.34; H, 3.02; N, 18.82. Found: C, 39.95; H, 2.99; N, 18.84.

### 4.1.5 | 7,15-bis(phenyl)-1,2,4,5,9,10,12,13-octaazacyclohexadeca-2,5,7,10,13,15-hexaene-3,11-dithiol (3B)

Light red powder; m.p. 196–198°C; Yield 63%; %; UV–Vis: 303, 395 nm; IR(KBr): ύ = 3250–3650 (broad) cm$^{-1}$ (NH), 1582 (s) cm$^{-1}$ (C=N), $^1$H-NMR (d6-DMSO): δ/ppm: 3.403 (s,2H,SH), 7.198–7.728 (m,8H, benzo-H), 8.089(s,2H, HC=C), 8.800(s,2H, HC=C), 10.869–10.914(d,J = 13.5 Hz, 2H,NH),12.834 (broad,2H,NH). $^{13}$C-NMR (d6-DMSO):

**TABLE 3** The synthesis of 7,15-bis(phenyl)-1,2,4,5,9,10,12,13-octaazacyclohexadeca-2,5,7,10,13,15-hexaene-3,11-dithiol and derivatives via the reaction of 2-substituted vinamidinium salts with thiocarbohydrazid in the presence of i-$Pr_2NEt$ in ethanol at 50°C



δ/ppm: 103.987, 125.591, 125.697, 126.248, 126.901, 129.241, 129.372, 129.928, 130.908, 138.717, 151.454, 167.182, Mass spectrum: m/e = 436 Anal. calcd for ($C_{20}H_{20}N_8S_2$): C, 55.04; H, 4.59; N, 25.69. Found: C, 54.87; H, 4.48; N, 25.73.

### 4.1.6 | 7,15-bis(4-methylphenyl)-1,2,4,5,9,10,12,13-octaazacyclohexadeca-2,5,7,10,13,15-hexaene-3,11-dithiol (4B)

Light red powder; m.p. 195–199°C; Yield 60%; UV–Vis: 330, 384 nm; IR(KBr): ύ = 3250–3650 (broad) $cm^{-1}$ (NH), 1579 (s) $cm^{-1}$(C=N), $^1$H-NMR (d6-DMSO): δ/ppm = 3.430(s,2H,SH), 7.491–7.828 (m,8H, benzo-H), 8.189(s,2H,HC=C), 8.908(s,2H, HC=C), 10.9469–10.991 (d,J = 13.8 Hz, 2H,NH),12.891 (broad,2H,NH). $^{13}$C-NMR (d6-DMSO): δ/ppm = 21.249, 106.827, 121.064, 121.916, 125.470, 125.591, 127.576, 128.824, 130.052, 132.427, 133.408, 139.931, 151.587, 164.276 Mass spectrum: m/e = 464, Anal. calcd for ($C_{22}H_{24}N_8S_2$): C, 56.89; H, 5.17; N, 24.14. Found: C, 56.68; H, 5.12; N, 24.18.

### 4.1.7 | 7,15-bis(3,5-dimethylpyridin)-1,2,4,5,9,10,12,13-octaazacyclohexadeca-2,5,7,10,13,15-hexaene-3,11-dithiol perchlorate (5B)

Brown powder; m.p. 192–195°C; Yield 70%; UV–Vis: 367, 410 nm; IR(KBr): ύ = 3250–3650 (broad) $cm^{-1}$ (NH), 1580 (s) $cm^{-1}$ (C=N), 1090 (s) $cm^{-1}$($ClO4^-$); $^1$H-NMR (d6-DMSO): δ/ppm = 2.531(s,12H), 3.291(s,2H,SH), 8.134–8.391 (m,6H, benzo-H), 8.894(s,2H,HC=C),), 9.219 (s,2H, HC=C), 11.170–11.209(d,J = 11.7 Hz,2H, NH),13.708 (broad,2H,NH), $^{13}$C-NMR (d6-DMSO): δ/ppm = 18.179, 110.742, 125.511, 126.932, 133.635, 138.331, 139.892, 141.716, 142.059, 145.259, 146.784, 160.766, Mass spectrum: m/e = 496 [M + -2ClO4-], Anal. calcd for 695 ($C_{22}H_{28}N_{10}S_2$)(ClO4-)2: C, 37.98; H, 4.03; N, 20.14. Found: C, 38.07; H, 3.98; N, 20.19.

### 4.1.8 | 7,15-bis(naphtalin)-1,2,4,5,9,10,12,13-octaazacyclohexadeca-2,5,7,10,13,15-hexaene-3,11-dithiol (6B)

Dark brown powder; m.p. 193–195°C; Yield 64%; UV–Vis: 345, 388 nm; IR(KBr): ύ = 3250–3650 (broad) $cm^{-1}$ (NH), 1575 (s) $cm^{-1}$ (C=N), $^1$H-NMR (d6-DMSO): δ/ppm:3.285 (s,2H,SH), 7.520–7.716 (m,8H, benzo-H), 7.766–7.910(m,2H,HC=C), 7.968–8.145 (m,6H, benzo-H), 8.573–8.575(d, J = 0.6 Hz, 2H, HC=C), 10.433–10.479 (d,J = 13.8 Hz, 2H,NH), 12.461 (broad,2H,NH). $^{13}$C-NMR (d6-DMSO): δ/ppm = 102.820, 121.574, 125.750, 126.510, 127.319, 127.612, 128.091, 128.775, 129.021, 129.417, 129.743, 130.260, 130.944, 131.151, 131.325, 131.962, 132.651, 132.627, 134.020, 135.174, 135.492, 138.553, 149.101, 164.587, Mass spectrum: m/e = 536, Anal. calcd for ($C_{28}H_{24}N_8S_2$): C, 62.68; H, 4.48; N, 20.89. Found: C, 62.75; H, 4.59; N, 24.27.

### 4.1.9 | 3,11-dimercapto-1,2,4,5,9,10,12,13-octaazacyclohexadeca-2,5,7,10,13,15-hexaene-7,15-diyl)bis (quinolin-1-ium) perchlorate(7B)

Dark brown powder; m.p. 201–203°C; Yield 61%; UV–Vis: 318 nm; IR(KBr): ύ = 3250–3650 (broad) $cm^{-1}$ (NH), 1583 (s) $cm^{-1}$ (C=N), 1080 (s) $cm^{-1}$(ClO4$^-$); $^{1H}$-NMR (d6-DMSO): δ/ppm = 3.396(s,2H,SH), 8.021–8.567 (m, 14H, benzo-H), 9.175(s,2H, HC=C), 9.667(s,2H, HC=C), 10.264(broad,2H,NH), 12.967 (broad,2H,NH). $^{13}$C-NMR (d6-DMSO): δ/ppm = 102.622, 121.340, 125.945, 126.574, 127.220, 127.664, 128.266, 128.859, 128.987, 129.177, 129.907, 130.354, 130.568, 131.037, 131.325, 131.495, 132.181, 133.919, 134.020, 138.012, 151.287, 166.822, Mass spectrum: m/e = 540 [M + -2ClO4-], Anal. calcd for 738 ($C_{26}H_{24}N_{10}S_2$)($ClO_4^-$)$_2$: C, 42.28; H, 3.25; N, 18.97. Found: C, 42.19; H, 3.29; N, 19.03.

### 4.1.10 | 3,11-dimercapto-1,2,4,5,9,10,12,13-octaazacyclohexadeca-2,5,7,10,13,15-hexaene-7,15-diyl)bis (isoquinolin-2-ium) perchlorate(8B)

Dark brown powder; m.p. 201–202°C; Yield 61%; UV–Vis: 319 nm;IR(KBr): ύ = 3250–3650 (broad) $cm^{-1}$ (NH), 1583 (s) $cm^{-1}$ (C=N), 1085 (s) $cm^{-1}$ (ClO4$^-$); $^{1H}$-NMR (d6-DMSO): δ/ppm = 3.859(s,2H,SH), 8.074–8.418 (m, 14H, benzo-H), 9.047(s,2H, HC=C), 10.128(s,2H, HC=C), 11.550(broad,2H,NH), 13.06 (broad,2H,NH). $^{13}$C-NMR (d6-DMSO): δ/ppm = 102.859, 121.325, 125.987, 126.495, 127.037, 127.568, 128.287, 128.622, 128.945, 129.119, 129.919, 130.409, 131.020, 131.340, 131.574, 132.822, 132.354, 133.907, 134.220, 138.054, 151.266, 166.181, Mass spectrum: m/e = 536, Anal. calcd for 738 ($C_{26}H_{24}N_{10}S_2$)($ClO_4^-$)$_2$: C, 42.28; H, 3.25; N, 18.97. Found: C, 42.32; H, 3.23; N, 18.93.

### 4.1.11 | 7,15-dichloro-1,2,4,5,9,10,12,13-octaazacyclohexadeca-2,5,7,10,13,15-hexaene-3,11-dithiol (9B)

Brown powder; m.p. 198–201°C; Yield 60%; UV–Vis: 305,340 nm;IR(KBr): ύ = 3250–3650 (broad) $cm^{-1}$ (NH), 1589 (s) $cm^{-1}$ (C=N), $^{1H}$-NMR (d6-DMSO): δ/ppm = 3.487(s,2H,SH), 8.074–8.133 (d,J = 17.7 Hz, 4H, HC=C), 11.688(broad,2H,NH), 13.071 (s,2H,NH). $^{13}$C-NMR (d6-DMSO): δ/ppm = 103.710, 138.543, 154.680, 160.702, Mass spectrum: m/e = 352, Anal. calcd for ($C_8H_{10}N_8S_2$)$Cl_2$: C, 27.27; H, 2.84; N, 31.82. Found: C, 27.33; H, 2.88; N, 31.76.

### 4.1.12 | 7,15-dibromo-1,2,4,5,9,10,12,13-octaazacyclohexadeca-2,5,7,10,13,15-hexaene-3,11-dithiol (10B)

Brown powder; m.p. 198–201°C; Yield 61%; UV–Vis: 309, 341 nm; IR(KBr): ύ = 3250–3650 (broad) $cm^{-1}$ (NH), 1587 (s) $cm^{-1}$ (C=N), $^{1H}$-NMR (d6-DMSO): δ/ppm = 3.486 (s,2H,SH), 8.070–8.109 (d,J = 11.7, 4H, HC=C), 11.683 (broad,2H,NH),12.995 (s,2H,NH). $^{13}$C-NMR (d6-DMSO): δ/ppm = 104.791, 138.568, 153.448, 166.550, Mass spectrum: m/e = 442, Anal. calcd for ($C_8H_{10}N_8S_2$)$Br_2$: C, 21.72; H, 2.26; N, 25.34. Found: C, 21.68; H, 2.24; N, 25.37.

### 4.1.13 | 7,15-bis(phenyl)-1,2,4,5,9,10,12,13-octaazacyclohexadeca-2,5,7,10,13,15-hexaene-3,11-dithiol complex (3C)

Ligand (L) (436 mg, 1 mmol.) was added to 25 mL ethanol and heated up to 50°C. Hot ethanolic solution (10 mL) of CoCl2.6H2O(237 mg, 1 mmol) or NiCl2.6H2O (237 mg, 1 mmol) or ZnCl2 (136 mg, 1 mmol.) was added to ligand solution with constant stirring. The mixture was refluxed for (5) hours at 50°C. A precipitate was formed. It was filtered, washed several times with EtOH, and then washed with diethyl ether and dried under vacuum at 50°C.

Ligand: Mass spectrum: m/e = 436 Anal. calcd for ($C_{20}H_{20}N_8S_2$): C, 55.04; H, 4.59; N, 25.69. Found: C, 54.87; H, 4.48; N, 25.73.

Complex-Co:

UV–Vis: 318, 337,421, 479 nm.

IR(KBr): ύ = 1425 cm-1 (C=N), 3390 cm-1 (NH), 683 cm-1 (M-N).

Complex-Ni:

UV–Vis: 339, 390 nm.

IR(KBr): ύ = 1448 cm-1 (C=N), 3392 cm-1 (NH), 673 cm-1 (M-N).

Complex-Zn:

UV–Vis: 295, 322 nm.

IR(KBr): ύ = 1504 cm-1 (C=N), 3397 cm-1 (NH), 685 cm-1 (M-N).

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## DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available in the supplementary material of this article.

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## SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

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