Synthesis and Characterization of a Novel Quinoxaline-Substituted *vic*-Dioxime and Its Complexes Containing Bis(12-Diazacrown-4) Derivatives

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A new quinoxaline-substituted vicinal dioxime ligand containing bis(12-diazacrown-4) units (**H_2L**) was synthesized by the reaction of cyanogen di-*N*-oxide with compound **4**. Mononuclear Ni^{II} and Cu^{II} complexes with a metal:ligand ratio of 1:2 for **H_2L** and a trinuclear Cu^{II} complex were also synthesized. The mononuclear Cu^{II} species coordinated to two Cu^{II} ions through the deprotonated oximate oxygens to yield a trinuclear structure *cis*-bridged by the oximate groups, with 1,10-phenanthroline as an end-cap ligand. The mononuclear Co^{III} complex of **H_2L** was isolated with pyridine and chlorine as axial ligands. In addition, a Co^{III} complex containing the BF_2^+ bridge macrocycle was synthesized using a precursor hydrogen-bridged Co^{III} complex via a template effect. The extraction abilities of **1**, **3**, and **11** were also evaluated in 1,2-dichloroethane by using several alkali (Li^+, Na^+, K^+, and Cs^+) and transition-metal picrates, such as Ag^+, Pb^{2+}, Cd^{2+}, Cu^{2+}, and Zn^{2+}. Structures of the ligands and metal complexes were solved by elemental analyses, ^1H and ^{13}C NMR, FT-IR, UV–vis, and mass spectra.

vic-Dioximes and their complexes have been widely investigated as analytical reagents,[1] models for biological systems such as vitamin B_{12},[2–4] compounds having columnar stacking which is thought to be the reason for their semiconducting properties,[5] and recently, reagents in macrocyclization reactions.[6–8] Due to the presence of mildly acidic hydroxy groups and slightly basic nitrogen atoms, *vic*-dioximes are amphoteric ligands, which form corrin-type square-planar, square-pyramidal, and octahedral complexes with transition-metal cations, such as Ni^{II}, Cu^{II}, Co^{II}, and Co^{III} as central atoms.[9,10] *vic*-Dioxime metal complexes, which began an area of coordination chemistry, have been widely explored during the past century.[9] Since that time, several quasi-macrocyclic and BF_2^+-capped oximes have been synthesized.[11,12] Incorporation of a *vic*-dioxime moiety on the macrocyclic provides an efficient binding site for transition-metal ions by formation of an MN_4 core with two additional hydrogen bridges.[13] Investigations of the redox properties of these types of complexes are also of great interest in terms of their various technological applications.[14–17] In previous papers, the synthesis of *vic*-dioxime ligands and their transition-metal complexes containing macrobicyclic derivatives,[18] monoaza crown ethers,[19] dithiadiazamacrocycles,[20] and diazacrown groups[21] have been reported.

The incorporation of nitrogen atoms into the macrocycle of crown ethers substantially extends the range of metallic and organic cations, with a high degree of specificity for particular cations dependent upon ring size and the nature of the heteroatoms that form complexes with such compounds.[22] Another useful property of nitrogen-containing crown ethers is that they provide considerable possibilities for relatively easy *N*-functionalization. Azacrown ethers thus modified have found applications in areas such as phase-transfer catalysis,[23] selective ion transport,[24] resolution of chiral molecules,[25] and to some extent, the study of electron transport.[22c]

In the present work, we report the synthesis and characterization of a (*E*,*E*)-dioxime containing bis(diazadioxa-12-crown-4 ethoxy) units and Ni^{II}, Cu^{II}, and Co^{III} complexes of **H_2L**. A trinuclear Cu^{II} complex and a Co^{III} complex containing the BF_2^+ bridge macrocycle were synthesized as well. In addition, alkali and heavy metal extraction abilities of **1**, **3**, and **11** were also examined.

Results and Discussion

Dinitro derivative **3** was synthesized in 91% yield (Scheme 1). The high yield obtained in this synthesis was attributed to the template effect of sodium cations. All spectral and physical data are in good accord with product **3**.

Amino derivative **4** was obtained from compound **3** as described in experimental section in 87.5% yield. This method is more advantageous than the others;[20] therefore, it was preferred. Amine derivative **4** was used for the following reaction without any further purification, because amino derivatives often decompose easily by light and heat. As it can be seen from experimental results, the synthesis were very satisfactory.

Novel quinoxaline substituted *vic*-dioxime ligand (**H_2L**) was synthesized from the reaction of compound **4** and cyanogen di-*N*-oxide **5** in yield 65%. In the ^1H NMR spectrum of **H_2L**, a single chemical shift for OH protons indicates that the oxime groups are in the *anti* form.[21,26] In the proton-decoupled ^{13}C NMR of **H_2L**, the carbon resonance of azomethine

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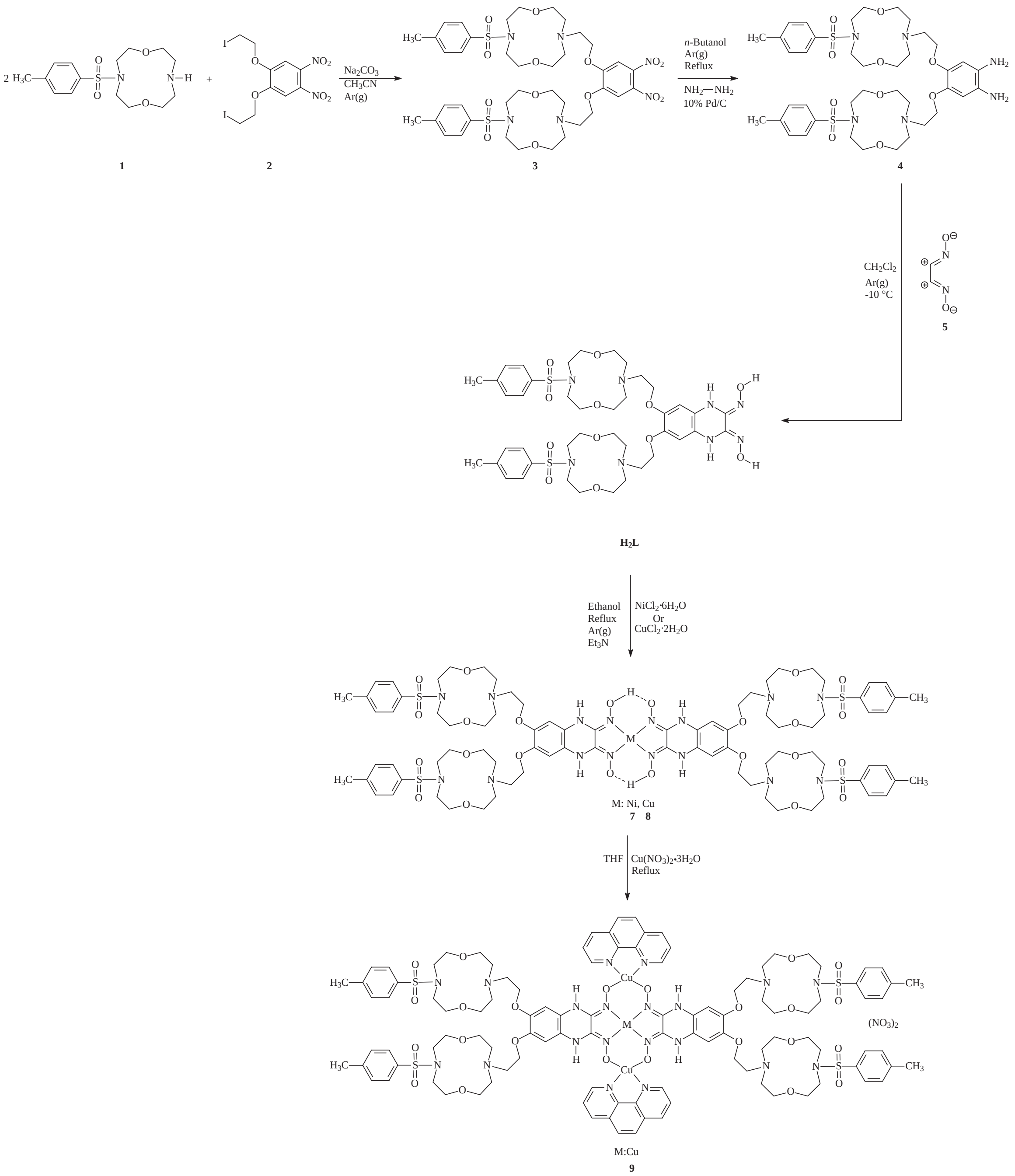
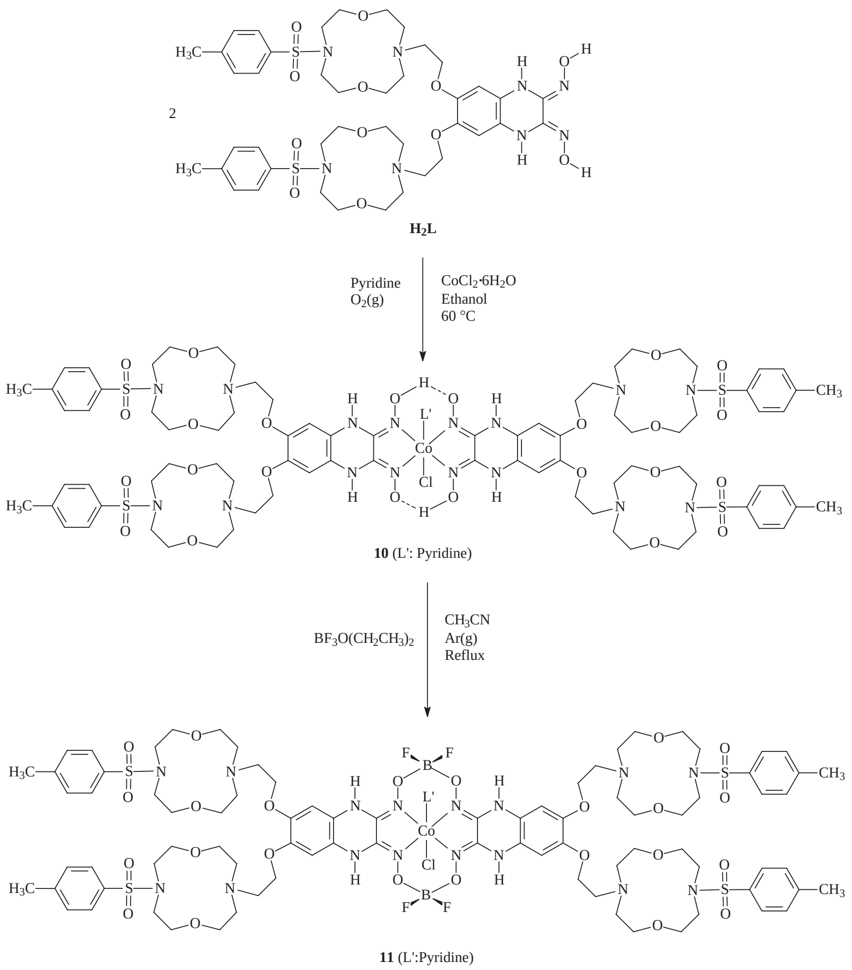


Scheme 1. Synthesis of **H_2L** and its mono- and trinuclear complexes.

group was found at lower field (151.1 ppm), and this unique signal for the oxime groups confirms the *anti* form of the *vic*-dioxime.[19] In the IR spectrum of **H_2L**, N–H, O–H, C=N, and N–O stretching vibrations were observed at 3385, 3245, 1638, and 938 cm^{-1}, respectively. These values are in agreement with the previously reported *vic*-dioxime derivatives.[18–21,26]

Mononuclear, $[Ni(HL)_2]$ (**7**) and $[Cu(HL)_2]$ (**8**) complexes were prepared from **H_2L** and stoichiometric amount of $NiCl_2 \cdot 6H_2O$ and $CuCl_2 \cdot 2H_2O$, respectively, in ethanol (Scheme 1). Both elemental analysis and FAB mass spectral data showed that metal:ligand ratio was 1:2 for compounds **7** and **8**. That C=N stretching vibrations of compounds **7** and **8** were lower than stretching vibration of **H_2L** (1638 cm^{-1}) proving that **H_2L** coordinates to Ni^{II} and Cu^{II} cations in *N,N′* fashion. Additionally, the disappearance of the signals for OH groups of **H_2L** at 1451 and 3245 cm^{-1} and the appearance of peaks at 1710 and 1729 cm^{-1} indicate that intramolecular hydrogen bonds form in compounds **7** and **8**. A singlet was observed at δ 16.68 in the ^1H NMR spectrum of square-planar complex **7**, showing the existence of intramolecular hydrogen bonds (O–H···O) which can be easily observed deuterium-exchange method.

We also synthesized a trinuclear Cu^{II} complex, $[Cu(L)_2(Cuphen)_2](NO_3)_2$ (**9**), (Scheme 1) with $(LH)_2Cu$ as the bridging ligand and 1,10-phenanthroline (phen) as an end-cap ligand. The secondary ions corresponding to the loss of two phenanthroline ligands together with two Cu and two nitrates



Scheme 2. Synthesis of complexes **10** and **11**.

appeared at $m/z = 1924.6$ $[M - (CuphenNO_3)_2]^+$. In the IR spectrum of **9**, no absorption attributable to a ν(O–H···O) vibration in the region 1600–2000 cm^{-1} indicates that the enolic hydrogen atoms are lost upon chelation. The stretching vibration, observed at 1645 cm^{-1}, was assigned to the C=N bond. This ν(C=N) vibration of the oxime for the trinuclear complex containing divalent metal cations was at a frequency significantly higher than that of the free ligand. This is in accord with the concept that, on trinuclear complex formation, the positively charged $Cu(phen)^{2+}$ unit stabilizes the negative charge on oxygen of the oximate function and thus increases the double bond character of the C=N bond.[27] In addition, IR spectroscopy indicates the presence of uncoordinated nitrate ions at 1375 cm^{-1}.[28]

Mononuclear Co^{III} complex, $[Co(HL)_2PyCl]$ (**10**), was prepared from $\mathbf{H_2L}$, pyridine and an equivalent amount of $CoCl_2 \cdot 6H_2O$ in the presence of ethanol (Scheme 2). According to elemental analysis data, the metal:ligand ratio was 1:2 for this complex and also pyridine and chlorine ligands were in axial positions of octahedral complex **10**. The singlet peak at δ 16.72 in ^{1}H NMR spectrum of octahedral complex **10** indicates the existence of intramolecular hydrogen bonds (O–H···O), which were verified using deuterium-exchange. Furthermore, chemical shifts for pyridine at δ 7.92, 7.52, and 6.98 indicate the existence of an octahedral complex **10**. Stretching vibrations of O–H functional group at 3245 cm^{-1} of $\mathbf{H_2L}$ disappeared, and a new peak was observed at 1718 cm^{-1}, which indicates of the existence of intramolecular hydrogen bonds. Broad C=N stretching vibration of compound **10** at 1624 cm^{-1} was lower than stretching vibration of $\mathbf{H_2L}$ (1638 cm^{-1}) proving that $\mathbf{H_2L}$ coordinates to Co^{III}.

BF_2-bridged Co^{III} complex **11** was obtained in high yield 68% at moderate dilution (0.2 mmol) with hydrogen-bridged Co^{III} complex **10** and boron trifluoride etherate (0.4 mmol) linking reagents (Scheme 2). This reagent readily reacted with the O–H···O bridge in the precursor molecule, yielding an extremely stable compound containing two O–BF_2–O bridges, and the axial pyridine ligand was retained, according to ^{1}H NMR and IR spectra and elemental analysis data of **11**. In the IR spectrum of the $BF_2{}^+$-capped Co^{III} complex, the C=N stretching region can be used to distinguish between the dihydrogen-bridged compound and the diboron-bridged compounds. This BF_2-macrocycle exhibited upward shifts of ca. 35 cm^{-1} due to the strong electron-withdrawing influence of the BF_2 groups incorporated in the macrocycle. The weak and broad band at 1718 cm^{-1}, corresponding the O–H···O in-plane deformation of the short hydrogen bond, disappeared upon encapsulation of the H-bonded complex, and peaks appeared around 1156–1030 and 871–840 cm^{-1} for the B–O and B–F groups, respectively.[29] In the ^{1}H NMR spectrum of

Table 1. Alkaline and Heavy Metal Picrate Extractions from Aqueous Solutions into 1,2-Dichloroethane by Using **1**, **3**, and **11**[a)]

Host molecule	Percent of metal picrate extracted/%[b)]								
	Li^+	Na^+	K^+	Cs^+	Ag^+	Zn^{2+}	Cd^{2+}	Cu^{2+}	Pb^{2+}
1	9.3 ± 0.1	42.3 ± 0.1	22.6 ± 0.1	0.4 ± 0.1	39.1 ± 0.1	27.5 ± 0.1	18.6 ± 0.1	36.7 ± 0.1	11.8 ± 0.1
3	12.9 ± 0.1	71.1 ± 0.1	42.3 ± 0.1	0.9 ± 0.1	63.8 ± 0.1	39.1 ± 0.1	27.4 ± 0.1	50.6 ± 0.1	24.2 ± 0.1
11	16.8 ± 0.1	77.6 ± 0.1	56.3 ± 0.1	4.1 ± 0.1	73.9 ± 0.1	43.7 ± 0.1	36.5 ± 0.1	60.3 ± 0.1	37.4 ± 0.1

a) Temperature 25 ± 1 °C; aqueous phase (10 mL), [picrate] $= 3.0 \times 10^{-3}$ M; organic phase (1,2-dichloroethane, 10 mL), [host molecule] $= 3.0 \times 10^{-3}$ M. b) Average and standard deviation for three independent measurements.

the BF_2^+-capped macrocycle, the deuterium exchangeable hydrogen-bridged protons belonging to the H-bonded pseudomacrocyclic precursor Co^{III} complex were no longer present after the formation of the BF_2 bridge.[19]

Solvent Extraction of Alkali and Heavy Metal Cations. In this work, besides the synthesis and characterization of a series of the new quinoxaline-substituted vicinal dioxime ligand **H_2L** and related complexes, we also investigated the alkali and heavy metal ion binding properties of the compounds having diaza-12-crown-4 units by solvent extraction of alkali and heavy metal picrates from the aqueous to an organic phase (Table 1). For comparison, the values obtained under the same conditions for *N*-tosyldiazadioxa-12-crown-4 (**1**) are included in Table 1. In addition to compound **3**, since the introduction of BF_2 groups to complex **10** leads to an increase in the solubility, in addition to the bulky diazacrown units, the BF_2-bridged Co^{III} complex **11** was used as a host. In the case of these host compounds, it might be expected that the capability of extracting lithium ion would be the highest among the alkali metal cations on comparing its size to the cavity size, because the diameter of the lithium ion is much more compatible with 12-membered macrocyclic units. However, the extraction was highest for the sodium ion due to the bis-crown effect. In other words, the sodium cation forms a sandwich-type complex by being bound between two diazacrown units with a metal:ligand ratio of 1:2. The capability of extraction for alkali metal cations increased with compounds **1**, **3**, and **11**. However, this increase was not so noteworthy as compared to the increase in the 12-membered macrocyclic units. This might be due to steric hindrance of the bulky diaza-12-crown-4 units.

In the course of this work, we compared extraction capabilities of two similar products: one is derived from nitro[21] and other one is derived from dinitro compound. We were not able to investigate extraction capability of **H_2L**, because of its moderate solubility under these conditions. Comparing **3** in this work to similar product **3** from our earlier work,[21] it is obvious that extraction capability of nitro derivative[21] is higher than that of dinitro derivative. Dinitro derivative **3** has two nitro functional groups, which have an electron-withdrawing effect greater than that of nitro derivative and decrease the donor character of the compound, causing a decrease in extraction capability as compared to the related nitro derivative.[21]

If we compare the BF_2-bridged Co^{III} complexes **10** from our earlier work[21] and **11** in our present work, the results are similar. Extraction capability increased with the number of *N*-tosyldiazadioxa-12-crown-4 units that can coordinate with more cations. Complex **10**[21] has more *N*-tosyldiazadioxa-12-crown-4 units than complex **11**, and therefore, its extraction capability is higher than that of **11**.

To the best of our knowledge, no extraction studies involving heavy metal cations compounds containing bis(diaza-12-crown-4) moieties except our earlier work[21] have been reported. One of our objectives was to investigate and perform such a sort of study. However, there are some reports about the extraction studies involving macrotricyclic molecules. According to these studies, molecules having diaza-12-crown-4 subunits form dinuclear complexes with Ag^I, Zn^{II}, and Cu^{II}. They can also form mononuclear complexes with other cations, such as Hg^{II}, Pb^{II}, and Cd^{II}.[30]

Aza-crown ethers form stable complexes with Ag^+ cation by replacement of O atoms with N atoms in crown ether moieties.[31c] As it can be seen from the Table 1, Ag^+ could be extracted the best because of the formation of M_2L-type complexes, i.e., more diaza-12-crown-4 units are available to bind to more cations that have small cation diameter. Also, the compounds having diaza-12-crown-4 units form ML-type complexes with the cations having bigger cation diameter. It means there are less diaza-12-crown-4 units per cation. Thus, the extraction capabilities of aza-crown ethers are lower for larger cations. In addition, from the data in Table 1, the aza-crown ether's ability to extract sodium and silver picrate are closely parallel. This can be attributed to the similarity in the diameters of Na^+ and Ag^+ cations.

Conclusion

In the course of this study, new precursor materials **3**, **4**, a new *vic*-dioxime ligand **H_2L**, containing bis(diaza-12-crown-4) moieties, and its [Ni^{II}, Cu^{II}, trinuclear Cu^{II}, Co^{III}, and BF_2-briged Co^{III}] complexes were synthesized in good yields and characterized. In addition, their cation-binding properties were evaluated using a solvent extraction technique and compared to our earlier work. The hosts from our earlier work have higher cation-binding capacities than those in this work. Picrate was used as counter anion all compounds.

The results obtained from the extraction experiments of alkali and heavy metal picrates indicated that the extraction capability of **11**, among bis(diaza-12-crown-4) moieties studied, was the best. The cation-binding abilities of **1**, **3**, **11** for Na^+ among alkali metals and Ag^+ among heavy metals were found to be the highest. The alkali and heavy metal ions extracting capabilities of bis(diaza-12-crown-4) moieties synthesized in this work follow the order **11** > **3** > **1**.

Experimental

Melting points were obtained on an electrothermal melting point apparatus and were uncorrected. The ^1H, ^{13}C NMR, and IR spectra were recorded on a Varian XL-200 spectrometer and on a Perkin-Elmer Spectrum One spectrometer with the samples in KBr pellets, respectively. The UV–vis spectra were recorded with a model Shimadzu 1601 UV–vis spectrometer using a 10 mm pathlength cell. Mass spectra were measured on a Varian MAT 711 and on Micromass Quatro LC/ULTIMA LC-MS/MS spectrometers using *m*-nitrobenzyl alcohol as the matrix. Elemental analysis of the compounds was determined on a CHNS-932 LECO instrument. The metal content of the complexes was determined with a Unicam 929 AA spectrophotometer.

Materials. 1,2-Bis(2-iodoethoxy)-4,5-dinitrobenzene,[31] 4-[(4-methylphenyl)sulphonyl)]-1,7-dioxa-4,10-diazacyclododecane,[32] and cyanogen di-*N*-oxide[33] were prepared according to the literature procedures. Reagent grade chemicals were used as received. Solvents were purified according to standard methods[34] before use. Silica gel (70–230 mesh) was used for chromatographic separations.

1,2-Bis(2-{4′-[4′-(methylphenyl)sulphonyl]-1′,7′-dioxa-4′,10′-diazacyclododecane}ethoxy)-4,5-dinitrobenzene (3). A three-necked flask fitted with a condenser was charged with finely ground anhydrous Na_2CO_3 (3.18 g, 30.00 mmol), compound **1** (1.968 g, 6.00 mmol), anhydrous NaI (0.45 g, 3.00 mmol), and dry acetonitrile (90 mL), then evacuated, refilled three times with argon, and connected to a vacuum line. Under argon, the mixture was stirred at 45 °C for 30 min. Compound **2** (1.524 g, 3.00 mmol) was added to this mixture under argon, and the reaction mixture was heated and stirred at 95 °C for 6 days. The reaction mixture was cooled to room temperature, and the precipitate was filtered off and washed with dichloromethane (25 mL). The filtrate and washes were combined, and the solvent was evaporated. The orange residue was dissolved in chloroform (7 mL), and ethanol was added until precipitation was first seen. The solution was then kept inside the refrigerator for overnight. The orange crystals that formed were collected by filtration and dried in vacuo. Yield: 2.48 g (91%); mp 290 °C. Anal. Found: C, 52.65; H, 6.44; N, 9.03%. Calcd for $C_{40}H_{56}N_6O_{14}S_2$: C, 52.86; H, 6.21; N, 9.25%. IR (KBr, cm^{-1}): 3045, 2928–2860, 1599, 1580–1540, 1463, 1380, 1275–1229, 1123–1040, 770, 743, 651. ^1H NMR ($CDCl_3$): δ 7.81 (d, 4H, Ar–H), 7.53 (d, 4H, Ar–H), 7.40 (s, 2H, Ar–H), 4.08 (t, 4H, Ar–O–CH_2), 3.77 (m, 16H, OCH_2), 3.29 (m, 16H, NCH_2), 2.78 (t, 4H, $NC\mathit{H}_2CH_2OAr$), 2.48 (s, 6H, Ar–CH_3). ^{13}C NMR ($CDCl_3$): δ 149.6 (ArCO), 145.8, 143.2, 134.7, 129.7, 127.1, 106.6, 69.3 (ArOC), 68.9–68.4 (OCH_2), 54.4 (NCH_2), 49.8 ($N\mathit{C}H_2CH_2OAr$), 21.0 (CH_3–Ar). MS (FAB positive): *m*/*z* 931.4 $[M + Na]^+$, 908.6 $[M]^+$.

1,2-Bis(2-{4′-[4′-(methylphenyl)sulphonyl]-1′,7′-dioxa-4′,10′-diazacyclododecane}ethoxy)-4,5-diaminobenzene (4). Compound **3** (2.48 g, 2.73 mmol) was dissolved in *n*-butanol (125 mL) at 60 °C under argon atmosphere and degassed on a vacuum line. Pd/C (10%) (0.160 g) was added to reaction mixture, and the mixture was heated at 150 °C. Hydrazinium hydrate (100%) (6.42 mL) was added to this mixture dropwise over 30 min while refluxing. The reaction mixture was filtered through Celite after 10 h and washed several times with *n*-butanol. The filtrate and washes were combined, and the solvent was evaporated to dryness under reduced pressure. Diethyl ether was added to the residue under argon, and the solution was kept in the dark, because the amino derivative can decompose. Little amount of amino derivative **4** was kept for IR, ^1H NMR, ^{13}C NMR, elemental analysis, and mass spectrums. Amine derivative **4** was used for the following reaction without any further purification. Yield: 2.03 g (87.5%); mp 244–246 °C. Anal. Found: C, 56.24; H, 7.30; N, 9.63%. Calcd for $C_{40}H_{60}N_6O_{10}S_2$: C, 56.58; H, 7.12; N, 9.90%. IR (KBr, cm^{-1}): 3406–3290 (NH_2), 3060–3032, 2980–2852, 1613 (NH_2, bending), 1595, 1542, 1471, 1362, 1277, 1162–1031, 913, 713, 698, 639. ^1H NMR ($CDCl_3$): δ 7.75 (d, 4H, TsArH), 7.36 (d, 4H, TsArH), 6.36 (s, 2H, Ar–CH), 4.45 (br s, 4H, NH_2), 3.98 (t, 4H, Ar–O–CH_2), 3.80 (m, 16H, $CH_2CH_2OCH_2CH_2$), 3.36 (m, 16H, –CH_2N), 2.75 (t, 4H, CH_2N), 2.40 (s, 6H, Ar–CH_3). MS (FAB positive): *m*/*z* 849.2 $[M]^+$.

H_2L (6). A cold solution −10 °C of cyanogen di-*N*-oxide (**5**), which was prepared from *anti*-dichloroglyoxime (0.35 g, 2.24 mmol) in dichloromethane (35 mL) and an aqueous solution of Na_2CO_3 (25 mL, 0.5 M), was added to a cold solution of compound **4** (1.90 g, 2.24 mmol) in dichloromethane (200 mL). The reaction was continued for 18 h at the same temperature and then evaporated to dryness. The crude product was crystallized from a dichloromethane/ethanol mixture (9:1) to yield pale brown crystals. Yield: 1.36 g (65%); mp 182–184 °C (dec). Anal. Found: C, 53.82; H, 6.64; N, 11.78%. Calcd for $C_{42}H_{60}N_8O_{12}S_2$: C, 54.07; H, 6.48; N, 12.02%. IR (KBr, cm^{-1}): 3385 (N–H), 3245 (O–H), 3082–3042, 2922–2857, 1638 (C=N), 1610, 1597, 1522, 1493, 1451, 1370, 1245, 1160–1015, 938 (N–O), 816, 714, 698, 549. ^1H NMR (DMSO-d_6): δ 10.30 (s, 2H, OH), 8.90 (s, 2H, NH), 7.69 (d, 4H, TsArH), 7.42 (d, 4H, TsArH), 6.91 (s, 2H, ArH), 4.12 (t, 4H, Ar–O–CH_2), 3.87 (m, 16H, $CH_2CH_2OCH_2CH_2$), 3.38 (m, 16H, –CH_2N), 2.75 (t, 4H, CH_2N), 2.36 (s, 6H, Ar–CH_3). ^{13}C NMR (DMSO-d_6): δ 151.1 (C=N–O–H), 147.2, 144.6, 142.7, 136.4, 131.2, 128.2, 104.8, 70.2 (ArOC), 68.2–67.9 (OCH_2), 53.5 (NCH_2), 49.6 ($N\mathit{C}H_2CH_2OAr$), 21.6 (CH_3–Ar). MS (FAB positive): *m*/*z* 933.2 $[M]^+$.

$[Ni(HL)_2]$ (7). A solution of $NiCl_2 \cdot 6H_2O$ (12 mg, 0.05 mmol) in ethanol (5 mL) was added to a solution of **H_2L** (93 mg, 0.1 mmol) in ethanol (25 mL) at 60 °C. A distinct change in color and a decrease in the pH of the solution (pH 2.39) was observed. While heating and stirring at the same temperature, ethanolic triethylamine (0.1 M, 2.74 mL) was added in order to increase pH 4.5–5.0. After heating the reaction mixture for 2 h in a water-bath, the precipitate was filtered off, and washed several times with water, ethanol, and diethyl ether, and then, orange-colored product was dried in vacuo over P_2O_5. Yield: 80 mg (84%); mp > 300 °C. Anal. Found: C, 52.18; H, 6.34; N, 11.79; Ni, 3.29%. Calcd for $C_{84}H_{118}N_{16}O_{24}S_4Ni$: C, 52.47; H, 6.19; N, 11.66; Ni, 3.06%. IR (KBr, cm^{-1}): 3385 (N–H), 3060–3018, 2970–2829, 1710 (O–H···O), 1622 (C=N), 1610, 1598, 1506–1449, 1380, 1276–1230, 1160–1025, 939 (N–O), 822, 713, 643. ^1H NMR (DMSO-d_6): δ 16.68 (s, 2H, O–H···O), 8.42 (br s, 4H, NH), 7.74 (d, 8H, TsArH), 7.35 (d, 8H, TsArH), 6.90 (s, 4H, ArH), 4.20–4.12 (m, 8H, Ar–O–CH_2), 3.95–3.84 (m, 32H, CH_2CH_2O-CH_2CH_2), 3.29–2.74 (m, 40H, –CH_2N), 2.39 (s, 12H, Ar–CH_3). MS (FAB positive): *m*/*z* 1922.3 $[M + 1]^+$.

$[Cu(HL)_2]$ (8). A solution of $CuCl_2 \cdot 2H_2O$ (9 mg, 0.05 mmol) in ethanol (5 mL) was added to a solution of **H_2L** (93 mg, 1 mmol) in ethanol (25 mL) at 60 °C. A distinct change in color and a decrease in the pH of the solution (pH 2.41) was observed. While heating and stirring at the same temperature, ethanolic triethylamine (0.1 M, 3.12 mL) was added in order to increase the pH to 5.0–6.0. After heating the reaction mixture for 2 h in a water-bath, the precipitate was filtered off and washed several times with water, ethanol, and diethyl ether, and then black-colored crystals were dried in vacuo over P_2O_5. Yield: 136 mg (76%); mp > 300 °C. Anal. Found: C, 52.92; H, 6.12; N, 11.62, Cu, 3.92%. Calcd for $C_{84}H_{118}N_{16}O_{24}S_4Cu$: C, 52.33; H, 6.18; N, 11.63, Cu, 3.30%. IR (KBr, cm^{-1}): 3390 (N–H), 3054–3021, 2940–2872, 1729 (O–H···O), 1620 (C=N), 1598, 1508–1446, 1373, 1245, 1170–1010, 941. MS (FAB positive): *m*/*z* 1927.6 $[M + 1]^+$.

$[Cu(HL)_2(CuL')_2](NO_3)_2$ (9). Complex **8** (0.482 g, 0.25 mmol) was suspended in THF (50 mL). A solution of 1,10-phenanthroline (0.099 g, 0.55 mmol) in THF (10 mL) and a solution of $Cu(NO_3)_2 \cdot 3H_2O$ (0.133 g, 0.55 mmol) in the same solvent (10 mL) were added to the above-mentioned suspension at reflux. The mixture was stirred and heated at reflux for 6 h under argon atmosphere. After that, the mixture was filtered, and the volume of filtrate was reduced to 5–10 mL on a rotary evaporator, and diethyl ether was slowly added with continuous stirring to the precipitated complex. The dark green product was filtered off, washed with water, ethanol, and diethyl ether, and dried in vacuo at room temperature. Yield: 0.152 g (24%); mp > 300 °C. Anal. Found: C, 51.57; H, 5.12; N, 11.85, Cu, 7.92%. Calcd for $C_{108}H_{132}N_{22}O_{30}S_4Cu_3$: C, 51.13; H, 5.24; N, 12.15, Cu, 7.52%. IR (KBr, cm^{-1}): 3395 (N–H), 3065, 3054–3020, 2980–2870, 1645 (C=N), 1598, 1506–1448, 1375 (NO_3), 1245 (Ar–O), 1130–1019 (C–O), 930 (N–O). MS (FAB positive): *m/z* 2535.3 $[M]^+$, 1924.6 $[M - (CuphenNO_3)_2]^+$.

$[Co(HL)_2L'Cl]$ (10). A solution of $CoCl_2 \cdot 6H_2O$ (24 mg, 0.1 mmol) in ethanol (10 mL) was added to a solution of **H_2L** (186 mg, 0.2 mmol) in ethanol (75 mL) at 60 °C by bubbling oxygen through the solution of **H_2L**. After 30 min, pyridine (0.01 mL, 0.1 mmol) in ethanol (5 mL) was added to mixture. Reaction mixture was heated and stirred for 6 h, while oxygen passing through it. Total volume of the residue was decreased to 1/4, and then precipitate was filtered off, washed several times with water, ethanol, and diethyl ether. Brown-colored product was then dried in vacuo over P_2O_5. Yield: 114 mg (56%); mp > 300 °C. Anal. Found: C, 52.14; H, 6.28; N, 11.85; Co, 3.12%. Calcd for $C_{89}H_{123}N_{17}O_{24}S_4CoCl$: C, 52.47; H, 6.08; N, 11.69; Co, 2.89%. IR (KBr, cm^{-1}): 3340 (N–), 3060, 3045, 2930–2890, 1718 (O–H···O), 1624 (C=N), 1601, 1597, 1549–1510, 1374, 1286–1226, 1159–1020, 943. ^1H NMR (DMSO-d_6): δ 16.72 (s, 2H, O–H···O), 8.25 (br s, 4H, NH), 7.92 (d, 2H, py–H), 7.64 (m, 8H, TsArH), 7.52 (t, 2H, py–H), 7.32 (m, 8H, TsArH), 6.98 (t, 1H, py–H), 6.87 (s, 4H, ArH), 4.24–4.06 (m, 8H, Ar–O–CH_2), 3.98–3.87 (m, 32H, $CH_2CH_2OCH_2CH_2$), 3.37–2.69 (m, 40H, –CH_2N), 2.36 (s, 12H, Ar–CH_3). MS (FAB positive): *m/z* 2037.8 $[M + 1]^+$.

$[Co(LBF_2)_2L'Cl]$ (11). A suspension of complex **10** (0.407 g, 0.2 mmol) in freshly distilled acetonitrile (100 mL) was brought to reflux under an argon atmosphere. $BF_3 \cdot OEt_2$ (0.1 mL, 0.4 mmol) was added to the above suspension, and the reaction mixture became red solution immediately. The solution was refluxed with stirring for 5 h and then allowed to cool to room temperature. The solvent was concentrated to 10 mL under reduced pressure. Dry Et_2O (20 mL) was then added dropwise, and the solution was allowed to stand at −18 °C overnight, whereupon the desired product precipitated. The claret red solid was collected by filtration, washed with cold acetonitrile and Et_2O, and then dried in vacuo. Yield: 290 mg (68%); mp > 300 °C. Anal. Found: C, 50.34; H, 5.42; N, 11.38; Co, 2.95%. Calcd for $C_{89}H_{121}N_{17}O_{24}S_4CoClB_2F_4$: C, 50.07; H, 5.67; N, 11.16; Co, 2.76%. IR (KBr, cm^{-1}): 3336 (N–H), 3060–3022, 2950–2863, 1645, 1605, 1590, 1545–1510, 1284–1223, 1156–1030 (B–O), 948, 871–840 (B–F). ^1H NMR (DMSO-d_6): δ 8.10 (br s, 4H, NH), 7.84 (d, 2H, py–H), 7.60 (m, 8H, TsArH), 7.49 (t, 2H, py–H), 7.38 (m, 8H, TsArH), 6.95 (t, 1H, py–H), 6.82 (s, 4H, ArH), 4.12–4.00 (m, 8H, Ar–O–CH_2), 3.92–3.85 (m, 32H, $CH_2CH_2OCH_2CH_2$), 3.24–2.74 (m, 40H, –CH_2N), 2.32 (s, 12H, Ar–CH_3). MS (FAB positive): *m/z* 2134.7 $[M + 1]^+$ and 2052.4 $[M - py\text{-}2]^+$.

Measurement of Alkali and Heavy Metal-Binding Properties of 1, 3, and 11. The extraction properties of **1**, **3**, and **11** were investigated under liquid–liquid phase and neutral conditions by using alkaline (Li^+, Na^+, K^+, and Cs^+) and heavy metal picrates (Ag^+, Pb^{2+}, Cd^{2+}, Cu^{2+}, and Zn^{2+}) as subsrates and measuring UV–vis the amounts of metal picrate in the aqueous phase before and after treatment with related compounds. Alkali metal picrates (3×10^{-5} M) were prepared by mixing alkali metal hydroxides and picric acid in deionized water, whereas heavy metal picrates were prepared by mixing metal nitrates and picric acid in deionized water. We also prepared 3×10^{-3} M solutions of related compounds (**1**, **3**, and **11**) in 1,2-dichloroethane. Then, equal volumes of both metal picrate solutions and compound solutions were added into plastic bottles, and the bottles were kept closed, and shaken for 12 h by shaker at 25 ± 1 °C. Finally, we took the aqueous phase and measured their absorbance at maximum wavelength (≈350 nm). For each combination of host and metal picrate, the picrate extraction was conducted on three different samples, and the average value of percent picrate extracted, with standard deviation, was calculated. The picrate extraction results are presented in Table 1. In the absence of host, blank experiment, no metal ion picrate extraction was detected. The extractability was determined based on the absorbance of picrate ion in the aqueous solutions. The extractability was calculated by using below equation;

$$E(\%) = [(A_{\text{before}} - A_{\text{after}})/A_{\text{before}}] \times 100, \qquad (1)$$

where A_{before} is the absorbance in the absence of ligand and A_{after} denotes the absorbance in the aqueous solution phase after extraction.

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