Nickel(II) and copper(II) complexes of aza macrocycles derived from trichloromethane

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Syntheses of nickel(II) complexes of the tetraaza macrocycles 2,7-dichloro-1,3,6,8-tetraazacyclodecane (DCCD) and 2,8-dichloro-1,3,7,9-tetraazacyclododecane (DICD) and a copper(II) complex of 2,6,8,12,13,17-hexaazabicyclo[5.5.5]heptadecane (HBCH) are reported in the template condensation of trichloromethane with 1,2-diaminoethane or 1,3-diaminopropane. Formulation of the synthesized products $[Ni(DCCD)(H_2O)_2]Cl_2$, $[Ni(DICD)(H_2O)_2]Cl_2 \cdot H_2O$, and $[Cu_3(HBCH)(H_2O)_6]Cl_6$, and the metal-free ligand hydrochloride HBCH · 6HCl has been confirmed by elemental analyses, conductivity measurements, and spectral studies. Potentiometric studies of nickel(II) and copper(II) complexes of HBCH and structurally similar 2,5,8,10,13,16,17,20,23-nonaazabicyclo[7.7.7]tricosane (NACT, earlier derived from trichloromethane and diethylenetriamine) have also been performed in the structural support of HBCH. In 1 : 1, metal : HBCH solution, copper(II) is coordinated to four N-donors of two-$HN(CH_2)_3NH–$ groups of the ligand in a non-planar tetraaza cavity. The equilibrium constant value ($\log K = 15.41$) for the reaction $Cu^{2+} + A \Leftrightarrow CuA^{2+}$ (A = HBCH) is in favor of the cyclic structure of the ligand. A high value ($\log K = 23.27$) for corresponding reaction in the NACT system is due to conformational change in the ligand, where copper(II) organizes the macrocycle to form a nearly planar cavity in which the cation fits well.

Keywords: Copper(II) and nickel(II) complexes; Tetraaza ligands; Cage ligands; Potentiometric study

1. Introduction

Macrocyclic compounds are similar in structure and reactions to many naturally occurring compounds, which are known to exhibit selective cation complexation [1–3]. Macrocycles are also useful in the separation of ions, phase transfer reactions, dissolution of metals and inorganic salts in organic solvents, ion selective electrodes, isotope separation, etc. [4]. A majority of macrocycles having 3–6 functional groups in the ring have been synthesized; rings consisting of 14-atoms and four donors with 3,2,3,2 bridge combination are very common [5–7]. The four almost equivalent N-donors are coordinated in a single plane about the metal ion.

Syntheses of transition metal complexes of new aza macrocycles with different cavity sizes, donor types, ring substituents, etc., under different experimental conditions have

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resulted in a large number and variety of compounds [8–12]. Recently, we reported syntheses of many complexes of new aza macrocycles derived from the template condensation of chlorocarbons with linear di-, tri-, and tetra-amines. The reaction of equimolar amounts of tetrachloromethane, diamines (1,2-diaminoethane and 1,3-diaminopropane), and nickel hydroxide in *n*-butanol led to the formation of mononuclear nickel(II) complexes of tetraaza ligands. Two molecules of amine and chlorocarbon are involved in the generation of planar rings, [10]-N_4 (bridge combination 2,1,2,1) and [12]-N_4 (bridge combination 3,1,3,1) in 1,2-diaminoethane and 1,3-diaminopropane systems, respectively [13]; about 50% of nickel hydroxide remains unreacted. A 10-membered tetraaza macrocycle is generated [14] in nickel-templated condensation between 1,2-diaminoethane and dichloromethane. But, the mode of cyclization is changed in the condensation of 1,2-diaminoethane with tetrachloro-, trichloro-, or dichloromethane in the presence of copper hydroxide with equimolar amounts of the reactants [15, 16]. The reaction yields penta-, tetra-, and tricopper(II) complexes of the larger macrocycles [25]-N_{10}, [20]-N_8, and [15]-N_6 in tetrachloro-, trichloro-, and dichloromethane systems, respectively. Further, a 1 : 1 : 1 reaction mixture of copper hydroxide, 1,3-diaminopropane, and tetrachloro- or dichloromethane yields dicopper(II) complexes of the planar tetraaza ring [12]-N_4 [14, 17].

Syntheses and subsequent study of macrocycles having more than one cyclic ring is interesting in interpreting the metal–donor bonding. Numerous polyoxa-macrobicyclic diamines encapsulate the metal ion in their central cavity [18, 19]. Since these ligands have three-dimensional arrangement of binding sites and can selectively encapsulate ions, the stability constants are usually higher than those of similar two-dimensional ligands [20, 21]. A number of polyaza-macrobicyclic cages have also been derived from 1,2-diaminoethane [22–24] and 1,2-diaminocyclohexane [25]. In recent years, efforts have been made to design and synthesize many new aza cage macrocycles capable to encapsulate one or more metal ions or other moieties [26, 27]. A bicyclic aza cryptand prepared by the condensation of 3,6-diformylpyridazine with tris(2-aminoethyl)amine has the capability to act as a binucleating host for hexa- or hepta-coordinated cations [28]. Synthesis of a tricopper(II) complex of a new type of cage macrocycle 2,5,8,10,13,16,17,20,23-nonaazabicyclo[7.7.7]tricosane (NACT) has also been reported recently [29] from an equimolar reaction mixture of diethylenetriamine, trichloro-methane, and copper hydroxide. Each copper(II) in the complex is coordinated to three aza donors and one water molecule. Many tricyclic N_{10}-cage macrocycles synthesized recently [30] have been found to encapsulate nickel(II) through only six aza donors. Their potentiometric measurements show an enhancement in stability constant over that of the corresponding tetraaza macrocycles. The enhancement in the value due to cage effect for these tricyclic systems decreases rapidly with increase in planar cavity size ([10]-$N_4 \rightarrow$ [14]-N_4). Thus, a high and comparable stability constant value is expected for planar tetraaza and spherical polyaza systems in which nickel(II) can be well fitted. However, studies on relative cation/anion and aza cage cavity sizes, the number and stereochemical arrangement of ligand binding sites, stability constants, and other related parameters in the interaction between the aza cages and transition metal cations are limited.

Here, we report the condensation of trichloromethane with 1,2-diaminoethane and 1,3-diaminopropane in the presence of nickel hydroxide. The condensed products from 2 : 2 : 1, trichloromethane, diamine, and nickel hydroxide reaction mixture are

mononuclear complexes of 2,7-dichloro-1,3,6,8-tetraazacyclodecane (DCCD) and 2,8-dichloro-1,3,7,9-tetraaza-cyclododecane (DICD). In view of unusual condensation reactions in the copper(II) system reported above, and particularly, generation of two different ligands, a 20-membered large ring macrocycle, and a new type of cage macrocycle in the condensation of trichloromethane with 1,2-diaminoethane and diethylenetriamine, respectively, a mixture of trichloromethane, 1,3-diaminopropane, and copper hydroxide (1 : 1:1) has been refluxed. The resulting product is a tricopper(II) complex of the cage macrocycle 2,6,8,12,13,17-hexaazabicyclo[5.5.5]heptadecane (HBCH) (figure 1).

Potentiometric studies on HBCH and structurally related NACT involving nickel(II) and copper(II) ions have also been performed. In 1:1, copper(II):HBCH solution, one copper(II) is coordinated to four N-donors (2, 6, 8, and 12) of two –HN(CH$_2$)$_3$NH– groups. A lower value of stability constant (log $K = 15.41$) for Cu^{2+} + A $\Leftrightarrow$ CuA^{2+} (A = ligand) than for tetraaza rings [12]-N$_4$ / [10]-N$_4$ (log $K \sim 22$) shows a negative cage effect probably due to metal coordination to only four N-donors of a small and nonplanar cavity and steric hindrance by uncoordinated -HN(CH$_2$)$_3$NH– group. Rotation of the free –HN(CH$_2$)$_3$NH– group through C(1)–N(13) and C(7)–N(17) may oppose accommodation of the metal ion in the cavity. An enhanced macrocyclic effect on stability constant is exhibited by the NACT system of larger spherical cavity. A high
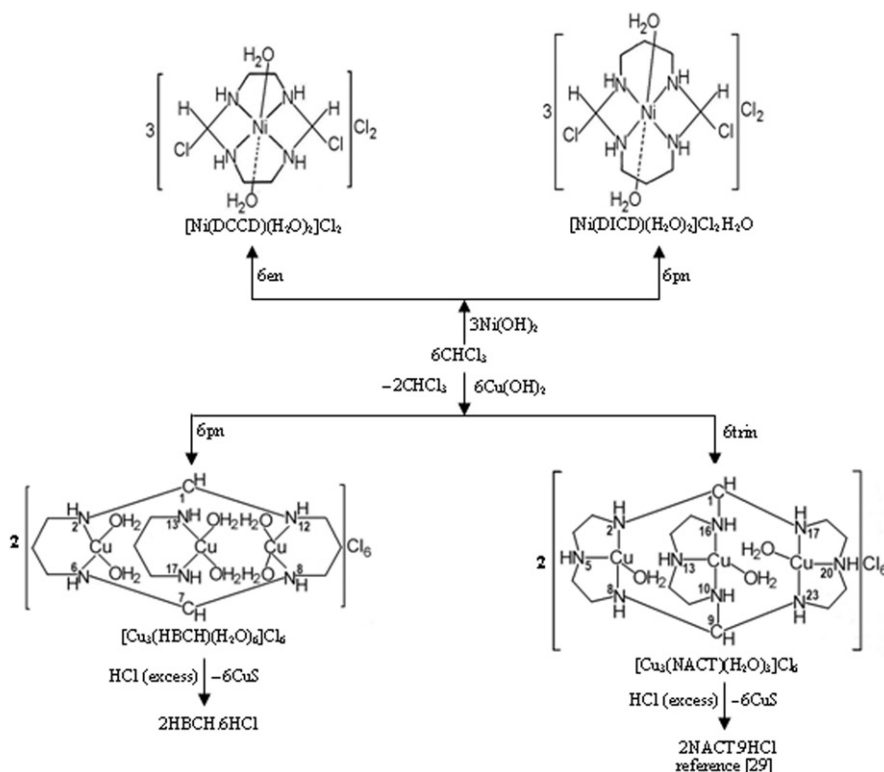
en = H$_2$N(CH$_2$)$_2$NH$_2$, pn = H$_2$N(CH$_2$)$_3$NH$_2$ and trin = H$_2$N(CH$_2$)$_2$NH(CH$_2$)$_2$NH$_2$

Figure 1. Reaction scheme.

stability constant ($\log K = 23.27$) for the corresponding reaction is expected due to conformational change where the metal ion organizes the ligand so that aza donors 2, 5, 8, and 13 are directed towards it and form a nearly planar cavity in which the cation fits well.

2. Experimental

2.1. *Materials*

Solvents and reagents used in the synthesis and solution studies of nickel(II) and copper(II) complexes were of reagent grade and used without purification.

2.2. *Physical and chemical measurements*

Microanalyses for carbon, hydrogen, and nitrogen were carried out at the Regional Sophisticated Instrumentation Centres, Central Drug Research Institute, Lucknow, and Punjab University, Chandigarh. The complexes were decomposed as described earlier [15] and metal content was determined by EDTA titrations [31]. Ionizable chlorides in the compounds were determined by conductometric titrations [15]. A DDR conductivity meter (Type 304) was employed for conductivity measurements. Magnetic susceptibilities were measured at room temperature on a Gouy balance using $CuSO_4 \cdot 5H_2O$ as calibrant. The electrospray mass spectrum (ESMS) of each macrocycle was recorded on a MICROMASS QUATTRO II Triple Quadrupole Mass Spectrometer. The sample dissolved in water was introduced into the ESI source through a syringe pump at the rate of $5 \mu L$ per min. The ESI capillary was set at 3.5 KV and the cone voltage was 40 V. The spectrum was collected in 6 s scans and the printouts are average of 6–8 scans. Infrared spectra (FTIR) from 4000 to $250\,cm^{-1}$ were recorded on a Perkin Elmer Infrared Spectrophotometer in KBr pellets at Punjab University, Chandigarh. Visible spectra of nickel(II) and copper(II) complexes were measured in their aqueous and methanolic solutions, respectively, using a Systronic Double Beam UV-Vis spectrophotometer-2202. The ^1H NMR spectrum was taken in D_2O solution and recorded on Bruker DRX 300 (300 MHz FT) using DSS as an internal standard.

2.3. *Potentiometric titrations*

The following aqueous mixtures: (i) 0.002159 N HNO_3; (ii) 0.0005 M $HBCH \cdot 6HCl/NACT \cdot 9HCl + (i)$; (iii) 0.0005 M copper nitrate/nickel nitrate + (ii); (iv) 0.001 M copper nitrate/nickel nitrate + (ii); and (v) 0.0015 M copper nitrate/nickel nitrate + 0.0005 M $NACT \cdot 9HCl + (i)$ were prepared and titrated against 0.1224 N NaOH solution using an EC 5656 pH meter with combined electrode system. The initial volume of each mixture was kept at 50 mL. The data were recorded at $25°C$ and at ionic strength of 0.10 M (KNO_3). From experimental data, titration curves (pH *vs.* moles of alkali used per mole of ligand, *a*) were plotted and analyzed [32, 33] to obtain information on metal–ligand equilibria in aqueous solution.

2.4. *Synthesis of nickel(II) complex of DCCD*

A mixture of nickel hydroxide (5.00 g, 53.92 mmole) and 1,2-diaminoethane (6.48 g, 107.82 mmole) prepared in 200 mL *n*-butanol turned into a light green solution after

being stirred for 5 min. Subsequently, trichloromethane (12.87 g, 107.80 mmole) was added and then refluxed for 15 min during which the following changes occurred in the mixture: light green turbidity disappeared, white turbidity formed, greenish-white, and then pinkish-white precipitate appeared in two steps and finally light pink precipitate was seen. The mixture was further refluxed for 2 h resulting in a pinkish-violet precipitate which was filtered and dissolved in 50 mL of water. The trace of light green residue of nickel hydroxide was removed by filtration. Concentration and refrigeration of the violet aqueous solution gave crude violet crystals of the product. The impurity was removed by washing the crystals with small volume of methanol, and finally with ether, and pure violet crystals were dried under reduced pressure (yield 5.80 g).

2.5. *Synthesis of nickel(II) complex of DICD*

Nickel hydroxide (5.00 g, 53.92 mmole) was added to a stirred solution of 1,3-diaminopropane (7.99 g, 107.78 mmole) in 150 mL of *n*-butanol. The mixture was stirred and heated for a few minutes which resulted in the formation of a light green turbid solution due to metal–ammine interaction. It was then cooled and trichloromethane (12.87 g, 107.81 mmole) was added and the whole content was stirred for 5 min. The mixture was refluxed for 3 h. The light green turbid solution gradually changed to a grey turbid solution, within 45 min of heating, and finally to violet solution with light grey precipitate. The condensed mixture was cooled and grey precipitate was removed by filtration. A known amount of water (60 mL) was added to the filtrate and the content was stirred for 2 min. The aqueous layer containing the macrocyclic product was separated from the non-aqueous layer. Crude violet crystals of $[Ni(DICD)(H_2O)_2]Cl_2 \cdot H_2O$ were obtained after concentration of the aqueous layer, and allowing the concentrated solution to stand for 2 weeks at room temperature. The product was recrystallized from methanol. A sticky material associated with the crystals as impurity was removed by 1 : 1, ether : benzene mixture, as described in many systems [34]. Analytically pure crystals were obtained by washing the product with methanol and finally with ether (yield 6.50 g).

2.6. *Synthesis of copper(II) complex of HBCH*

A mixture of 1,3-diaminopropane (6.08 g, 82.02 mmole) and copper hydroxide (8.00 g, 82.00 mmole) in 200 mL methanol was stirred and heated for a few minutes. To the resulting deep blue solution consisting of a small amount of greenish-blue residue, trichloromethane (7.79 g, 82.01 mmole) was gradually added with constant stirring. The whole content was then refluxed for 4 h. The condensed dirty blue turbid mixture was filtered, and the trace of blackish-brown residue was discarded. The dull blue methanolic solution was kept for crystallization. Shining light blue crystals of the product were collected after the solution was allowed to stand at room temperature for 4 days. The crystals were found to be analytically pure and were used without further purification (yield 2.80 g).

2.7. *Preparation of metal-free macrocycle HBCH · 6HCl*

An aqueous solution of $[Cu_3(HBCH)(H_2O)_6]Cl_6$ in 100 mL of water was prepared by dissolving 1.50 g (1.99 mmole) of the complex. The solution was acidified with

concentrated HCl (5 mL, 12 N) and H_2S gas was passed for ~15 min. The CuS formed was separated by filtration and the presence of copper(II) in the filtrate was checked again by passing H_2S gas into it. The filtrate was further boiled for 2–3 min in order to remove the dissolved H_2S. The filtrate containing the hydrochloride of the macrocycle was concentrated and kept at room temperature (25°C, for 15 days) for crystallization. Needle-shaped white crystals were washed with ether, and dried under reduced pressure (yield 0.70 g).

3. Results and discussion

3.1. *Synthesis*

Condensation of 1,2-diaminoethane and 1,3-diaminopropane with trichloromethane in the presence of nickel hydroxide in 2:2:1 molar ratio yielded nickel(II) complexes of 10- and 12-membered macrocycles DCCD and DICD, respectively. Initially a 1:2, nickel:ammine complex is formed which then condenses with two molecules of the chlorocarbon to yield mononuclear product $[Ni(DCCD)(H_2O)_2]Cl_2$ or $[Ni(DICD)(H_2O)_2]Cl_2$. Under similar conditions, nickel-templated condensation of 2:2 dichloromethane and 1,2-diaminoethane also yielded [14] a mononuclear nickel(II) complex of 1,3,6,8-tetraazacyclodecane (TACD, [10]-N_4, bridge combination 2,1,2,1). Synthesis of nickel(II) complexes of 2,2,7,7-tetrachloro-1,3,6,8-tetraazacyclodecane (TTCE, [10]-N_4, bridge combination 2,1,2,1) and 2,2,8,8-tetrachloro-1,3,7,9-tetraazacyclododecane (TTDE, [12]-N_4, bridge combination 3,1,3,1) reported [13] in the template condensation of equimolar diamines (1,2-diaminoethane and 1,3-diaminopropane), carbon tetrachloride and nickel hydroxide are also in structural support of the generated tetraaza macrocycles DCCD and DICD and their nickel(II) complexes.

In an equimolar reaction mixture of 1,3-diaminopropane, trichloromethane, and copper hydroxide, a new cage macrocycle HBCH is generated involving the condensation of three molecules of 1,3-diaminopropane with two molecules of trichloromethane. Thus, a trinuclear copper(II) complex $[Cu_3(HBCH)(H_2O)_6]Cl_6$ is formed where each copper(II) in square planar environment is surrounded by two aza donors and two water molecules. However, when trichloromethane was replaced by tetrachloromethane under similar experimental conditions, only a tetraaza planar macrocycle TTDE was generated [17]. Perhaps, an additional Cl in tetrachloromethane (larger than H) opposes the condensation of three 1,3-diaminopropanes with two molecules of tetrachloromethane to yield the tricopper(II) complex of 1,7-dichloro-2,6,8,12,13,17-hexaazabicyclo[5.5.5]heptadecane. Synthesis of a trinuclear copper(II) complex of the similar macrocycle NACT reported recently [29] in the template condensation of equimolar mixture of trichloromethane, diethylenetriamine, and copper hydroxide and also favors the generation of HBCH.

Planar tetraaza cavity of 1,3,7,9-tetraazacyclododecane (TADD) [14] or TTDE [17] accommodates two copper(II) ions, but, in HBCH none of the three fused tetraaza rings is planar; therefore accommodation of three copper(II) ions in the cavity of HBCH appears unusual. However, coordination may occur if none of the three planes consisting of copper and a pair of nitrogen donors N(2)–N(6), N(8)–N(12), or N(13)–N(17) passes through the center of the spherical cavity of the cage. However,

there may be a possibility of expansion of the smallest cavity to larger cavity systems (structures II (a or b), III (a or b), IV (a, b, or c), and V (a or b)) involving the condensation of 4 : 6, 6 : 9, 8 : 12, 10 : 15, etc., molecules of trichloromethane and 1,3-diaminopropane, respectively, to avoid crowding of copper(II) ions in the spherical cavity. However, generation of the corresponding large structure is not favored in the 1,2-diaminoethane system. The smallest planar macrocycle 1,3,6,8-tetraazacyclodecane and the smallest cage 2,5,7,10,11,14-hexaazabicyclo[4.4.4]tetradecane if formed, cannot accommodate two and three copper(II) ions, respectively, in their cavities and therefore, a [20]-N_8 planar macrocycle is generated which accommodates four copper(II) ions in its cavity [16].
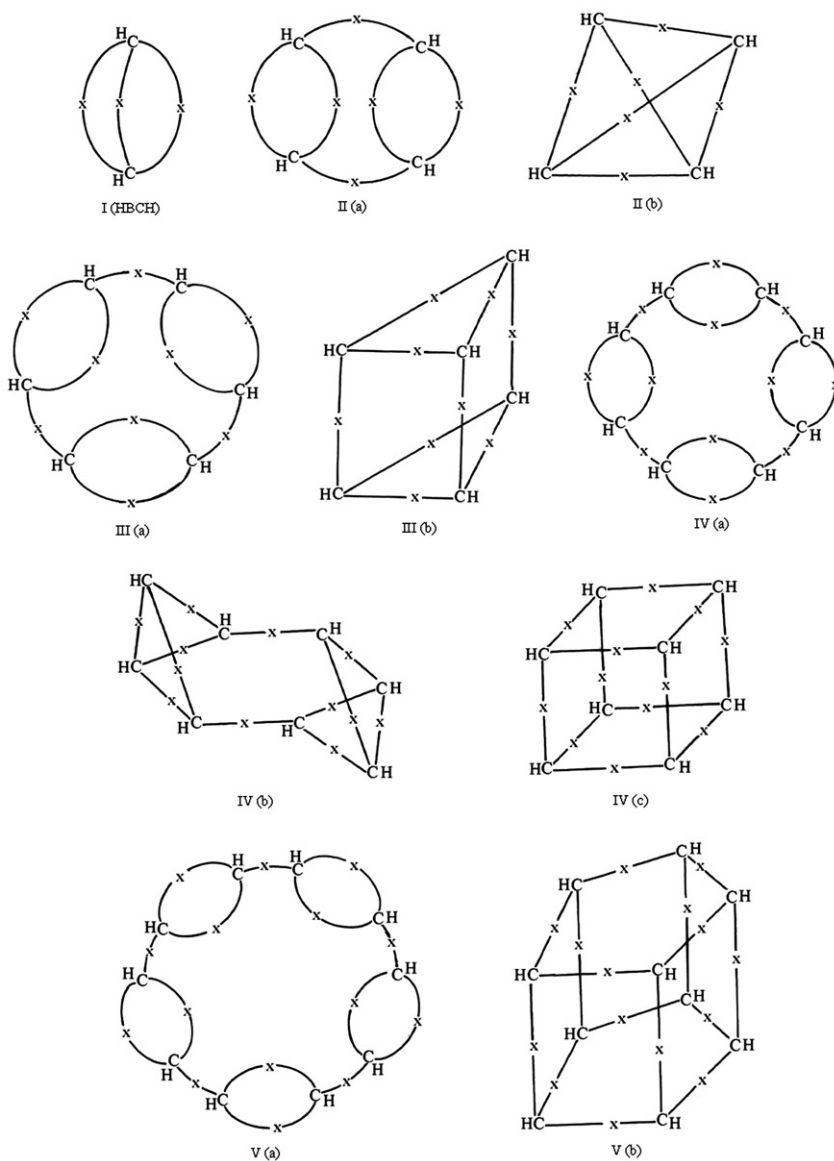
Elemental analyses, conductivity measurements, and spectral studies support the formation of new macrocyclic compounds (table 1). The IR results are strongly suggestive of the cyclic nature of the products [10, 30, 31]. Among various proposed cage structures (I–V) in copper(II)-templated condensation reactions of trichloromethane with 1,3-diaminopropane, structure I has been confirmed by potentiometric studies and the mass spectrum of the complex.

3.2. *Infrared spectra*

Evidence of cyclization of nickel(II) complexes of DCCD and DICD is demonstrated by the absence of absorption bands from $-NH_2$. The N–H stretch of secondary amine appears as a weak but sharp peak at $3166 \, cm^{-1}$ in the infrared spectrum of the nickel(II) DCCD complex. The corresponding peak in DICD system is a sharp shoulder at $3150 \, cm^{-1}$. The N–H bend in DICD system is at higher energy ($1595 \, cm^{-1}$) than in the DCCD system ($1570 \, cm^{-1}$). Coordination of the macrocyclic ligand through nitrogen is indicated by very weak and medium intensity peaks at 444 and $480 \, cm^{-1}$ in DCCD and DICD systems, respectively. The infrared spectrum of the nickel(II)–DCCD complex includes strong but sharp peaks at 3284 and $659 \, cm^{-1}$ that are assigned to stretching and wagging vibrations of coordinated water. Similarly, water coordination in nickel(II)–DICD complex is supported by the presence of a broad band at $3250 \, cm^{-1}$ (ν(H–O)) and bands at 800 and $628 \, cm^{-1}$ attributed to rocking and wagging, respectively. Bands at 521 (medium but broad) and $520 \, cm^{-1}$ (very weak but sharp) in DCCD and DICD systems, respectively, are assigned to ν(Ni–O) of coordinated water. Medium bands at 2947 and $2885 \, cm^{-1}$ (DCCD system) or 2920 and $2870 \, cm^{-1}$ (DICD system) are due to C–H asymmetric and symmetric stretching vibrations, respectively. A low-energy medium band in the DCCD system at $1458 \, cm^{-1}$ or a weak but very sharp band in the DICD system at $1438 \, cm^{-1}$ is attributed to C–H scissoring vibration.

The infrared spectrum of $[Cu_3(HBCH)(H_2O)_6]Cl_6$ exhibits a N–H stretching shoulder of secondary amine at $3120 \, cm^{-1}$. The δ(N–H) is at $1585 \, cm^{-1}$. Bands at 1085 and $492 \, cm^{-1}$ are assigned to ν(C–N) and ν(Cu–N), respectively. The C–H asymmetric, symmetric stretching, and scissoring are seen at 2920, 2870, and $1400–1300 \, cm^{-1}$ (very broad), respectively. The presence of coordinated water molecule is indicated by a strong but very broad peak at $3250 \, cm^{-1}$ followed by strong/medium but sharp peaks at 660 and $590 \, cm^{-1}$ attributed to O–H stretching, wagging and ν(Cu–O), respectively. Other bands at 2390, 1270, 1180, 1145, 1020, 910, 880, 812, 492, 450, and $386–372 \, cm^{-1}$ are associated with the skeletal vibrations of the complex. A single weak but high energy band in the infrared spectrum of metal-free ligand hydrochloride at $3228 \, cm^{-1}$ is assigned to ν(N–H). Medium but sharp δ(N–H) and ν(C–N) bands are observed at 1601 and $1101 \, cm^{-1}$, respectively. The asymmetric and symmetric stretching and scissoring vibrations of C–H are seen at 2970, 2893, and $1466 \, cm^{-1}$, respectively. A number of weak or very weak bands at 2773, 2654, 2653, 2492, 2405, 2302, and $2249 \, cm^{-1}$ and prominent medium but very sharp band at $2015 \, cm^{-1}$ are associated with $>NH_2^+Cl^-$ group.

Table 1. Analytical and physical data of the macrocyclic compounds.

Compound	Yield (%) color	Color at d.p. (m.p. °C)	Λ_M (Ohm^{-1}cm^{2}mol^{-1})	% Found (Calcd)					Molecular weight found (Calcd)
				C	H	N	Ni/Cu	Cl[c]	
[Ni(DCCD)(H$_2$O)$_2$]Cl$_2$ NiC$_6$H$_{18}$N$_4$O$_2$Cl$_4$	28.4 Violet	Dark violet[a] (124)[d]	250	18.98 (19.02)	4.82 (4.80)	14.84 (14.79)	15.54 (15.50)	18.76 (18.72)	375 (378.8)
[Ni(DICD)(H$_2$O)$_2$]Cl$_2$·H$_2$O NiC$_8$H$_{24}$N$_4$O$_3$Cl$_4$	28.4 Violet	Light violet[b] (120)[d]	240	22.53 (22.61)	5.68 (5.71)	13.15 (13.19)	13.78 (13.82)	16.70 (16.69)	402 (424.9)
[Cu$_3$(HBCH)(H$_2$O)$_6$]Cl$_6$ Cu$_3$C$_{11}$H$_{38}$N$_6$O$_6$Cl$_6$	13.59 Light blue	Black (195)[d]	580	17.72 (17.67)	5.03 (5.04)	11.13 (11.16)	25.37 (25.30)	28.15 (28.23)	745.0 (753.49)
HBCH·6HCl C$_{11}$H$_{26}$N$_6$·6HCl	93.3 White	Black (210)[d]	–	28.71 (28.65)	7.03 (7.01)	18.27 (18.23)	–	46.00 (46.12)	386.0 (461.2)

[a]Brownish black at 228–268°C, brownish black liquid at 295°C.
[b]Brownish black at 225–270°C.
[c]Ionizable chloride ions.
[d]Decomposition point.

3.3. *Comparison of DCCD, DICD, and related systems*

Ring cavities of DCCD and DICD are comparable with those of TTCE (bridge combination 2,1,2,1) and TTDE (bridge combination 3,1,3,1) [13], respectively. The ν(Ni–N) in complexes with nickel(II) follows the trend DICD > TTDE (ν(Ni–N), 470 cm^{-1}) and DCCD > TTCE (ν(Ni-N), 442 cm^{-1}). The low-frequency vibrations in TTDE and TTCE as compared to that in DICD and DCCD, respectively, are due to additional Cl's present in TTDE and TTCE. The Ni–N bond order from infrared vibrational frequencies of the metal complexes of these macrocycles in general follows the trend DICD > TTDE > DCCD > TTCE. Thus, metal ion is more suitably fitted in a ring cavity of 3,1,3,1 bridge combinations than in the smallest cavity of 2,1,2,1 bridge combination. A parallel result has recently been reported [14] for copper(II), which favors the coordination of a cavity of bridge combination 3,1,3,1 of the macrocycle 1,3,7,9-tetraazacyclododecane (TADD), as compared to that of bridge combination 2,1,2,1 of the macrocycle 1,3,6,8-tetraazacyclodecane (TACD). The ν(Cu–N) in TADD and TACD complexes with copper(II) (mononuclear) are at 488 and 468 cm^{-1}, respectively.

3.4. *Comparison of HBCH and related systems*

There is close correspondence in spectra of HBCH and TADD, probably due to structural similarity. Two and three –NH(CH$_2$)$_3$NH– groups are joined with –CH$_2$– and >CH– groups in TADD and HBCH, respectively, with intensity higher in HBCH due to more –CH$_2$– groups. Similar infrared vibrations for the two macrocycles also support the absence of Cl in HBCH. The ν(Cu–N) in [Cu$_3$(HBCH)(H$_2$O)$_6$]Cl$_6$ is at higher frequency than that in [Cu$_2$(TADD)(H$_2$O)$_4$]Cl$_4 \cdot$ 2H$_2$O (442 cm^{-1}) [14]. In these tri- and dinuclear complexes, each copper(II) is coordinated to two nitrogens of the corresponding macrocyclic rings. Also, ν(Cu–O) in HBCH complex of copper(II) is comparatively at higher frequency (590 cm^{-1}) as compared to that in the dinuclear complex of TADD (588 cm^{-1}). There is large shifting of ν(N–H) and ν(C–N) vibrational frequencies in the tri- and dinuclear complexes of HBCH and TADD, respectively, from those in the corresponding ligands. Lowering of each vibration in trinuclear complex is larger than that in the dinuclear complex. This unusual feature of HBCH complex is probably associated with the 3-D cage structure which encapsulates the metal ion as well as the coordinated water molecules. Further, the ν(Cu–N) (522 cm^{-1}) and ν(Cu–O) (629 cm^{-1}) recorded [29] for tricopper(II) complex of 3-D ligand NACT are at higher frequencies than the corresponding vibration for the tricopper(II) complex of HBCH. It indicates that copper(II) ion and coordinating H$_2$O molecules are well fitted in the spherical cavity of NACT than those in the cavity of HBCH. In addition, in NACT system each copper(II) ion is coordinated to three N-donors in the cavity.

3.5. *Electronic spectra*

Electronic spectral measurements are useful in distinguishing geometries of the complexes. A majority of nickel(II) complexes [3, 35–37] are square-planar but, those of ligands with pendant donors [3], cage systems consisting of additional aza donors

[30], and large ring macrocycles [38, 39] are generally octahedral. The spectra of nickel(II) complexes of the small ring macrocycles DCCD and DICD studied here are very similar with three absorption bands at $\sim$12,500 ($\varepsilon \sim 7$), $\sim$18,650 ($\varepsilon \sim 7$), and $\sim$29,000 cm^{-1} ($\varepsilon \sim 8$), attributed to d–d transition and assigned to $^3A_{2g} \rightarrow {}^3T_{2g}$, $^3A_{2g} \rightarrow {}^3T_{1g}(F)$, and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ of octahedral nickel(II) [40]. The octahedral geometry is further confirmed by the paramagnetic nature of the complexes. The four aza donors of the ring are coordinated to nickel(II) in a single plane and two water molecules are at axial sites.

Square-planar or rectangular planar copper(II) tetraaza macrocycles usually exhibit a single broad d–d band near 20,000 cm^{-1} ($\varepsilon \sim 125$) [41]. Cummings *et al.* [42] have reported a comparatively low-energy broad absorption band in the visible region centered at 18,000 cm^{-1} ($\varepsilon \sim 250$) for the copper(II) complex of the neutral ligand 11,13-dimethyl-1,4,7,10-tetraazacyclotrideca-10,13-diene. Many other neutral diimines have been reported [43] to form square-planar copper(II) complexes. Their visible spectra show only one broad band. A similar trend with a single broad band at 19,600 cm^{-1} ($\varepsilon \sim 320$) is followed in copper(II)–HBCH complex where each copper(II) ion in square-planar environment is coordinated to two aza donors of the ligand and two H_2O.

3.6. ^1H NMR spectrum

The broad triplet and multiplet at 3.16 and 2.01 ppm, respectively, attributed to α- and β-methylene protons, are observed in the spectrum of HBCH · 6HCl. Position is in agreement with the integrations of the signals (proton ratio 16 : 8). The NH_2^+ proton is centered at 5.00 ppm. The CH resonance is probably obscured by the NH_2^+ protons.

3.7. Mass spectra

The highest m/z value (ESMS) of each system is slightly low from the molecular weight of the macrocycle associated with mass lost (H/HCl) due to the fragmentation of the molecular ion (table 1). The molecular ion peak in $[Ni(DCCD)(H_2O)_2]Cl_2$ and $[Ni(DICD)(H_2O)_2]Cl_2 \cdot H_2O$ spectra are very weak. However, the peaks corresponding to the macrocycles at m/z 211 and 238, respectively, for $[DCCD - H]^+$ and $[DICD - 2H]^+$ ion confirm the formation of the complexes [44–46]. Similarly, a peak appears in the spectrum of $[Cu_3(HBCH)(H_2O)_6]Cl_6$ at m/z 240 for metal free $[HBCH - 2H]^+$. The spectrum of $[Cu_3(HBCH)(H_2O)_6]Cl_6$ and its structural fragmentation are shown in "Supplementary material".

The spectrum of the copper(II) complex has been further analyzed on the basis of isotopic abundance of different nuclei, particularly those of copper (Cu-63, 69% and Cu-65, 31%) and chlorine (Cl-35, 76% and Cl-37, 24%). The isotopic abundances for the combination of copper and chlorine atoms calculated by binomial expansion show a typical pattern of peaks (figure 2). The number of peaks increases with increase in the combined number of coppers and chlorines. $[Cu_3(HBCH)(H_2O)_6Cl_6 - 8H]^+$ shows a very weak peak corresponding to the molecular ion at m/z 745 (3.09%). The assignment of this peak is supported by the isotopic distribution, as shown in figure 2 for a combination of 3Cu and 6Cl's, which spans from m/z 741 to 755. The second highest peak at m/z 723 spans from m/z 719 to 728 due to $[Cu_3(HBCH)(H_2O)_5Cl_6 + 6H]^+$.
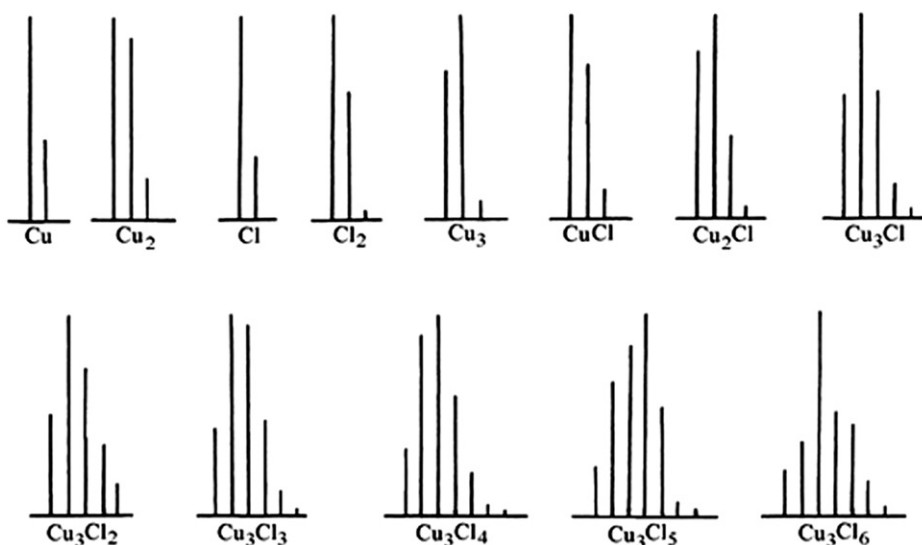
Figure 2.   Isotopic abundances for combinations of copper and chlorine atoms.

There are 5–7 weak/very weak peaks separated by two mass units for the fragments (m/z 696 $[Cu_3(HBCH)(H_2O)_3Cl_6 - 3H]^+$, m/z 669 $[Cu_3(HBCH)(H_2O)Cl_6 + 6H]^+$, m/z 644 $[Cu_3(HBCH)Cl_6 - H]^+$, m/z 624 $[Cu_3(HBCH)(H_2O)Cl_5 - 6H]^+$, m/z 597 $[Cu_3(HBCH)(H_2O)Cl_4 + 4H]^+$, m/z 536 $[Cu_3(HBCH)Cl_3 - 2H]^+$, and m/z 509 $[Cu_3(HBCH)Cl_2 + 6H]^+$). The number of peaks is almost in agreement, as shown in figure 2, for a combination of three coppers and 2–6 chlorines. The number of isotope peaks for other fragments: m/z 462 $[Cu_3(HBCH)Cl - 6H]^+$ (five); m/z 482 $[Cu_3(HBCH)(H_2O)Cl - 4H]^+$, or m/z 408 $[Cu_2(HBCH)Cl + 3H]^+$ (four); m/z 451 $[Cu_3(HBCH)(H_2O)]^+$, m/z 435 $[Cu_3(HBCH) + 2H]^+$, m/z 381 $[Cu_2(HBCH)(H_2O) - 5H]^+$, m/z 372 $[Cu_2(HBCH) + 4H]^+$, m/z 360 $[Cu(HBCH)(H_2O)Cl + 2H]^+$ or m/z 345 $[Cu(HBCH)Cl + 5H]^+$ (three), and m/z 295 $[CuC_{11}H_{25}N_5 + 5H]^+$ or m/z 246 $[CuC_8H_{19}N_5 - 2H]^+$ (two) support isotopic abundances, as shown in figure 2. Three peaks at m/z 309 support $[(HBCH)Cl_2 - 3H]^+$ where peaks due to $[Cu(HBCH) + 4H]^+$ are in the background. Similarly, two peaks at m/z 276 may be regarded due to $[CuC_{10}H_{23}N_5]^+$ and $[(HBCH)Cl - H]^+$.

3.8. Solubility, conductivity, and other data

The nickel complex of DCCD and DICD have low decomposition points (table 1), whereas $HBCH \cdot 6HCl$ and $[Cu_3(HBCH)(H_2O)_6]Cl_6$ are thermally stable, decomposing near their melting points. All the complexes are highly soluble in water due to their ionic nature; most are soluble in other polar solvents like methanol, ethanol, DMF, DMSO, etc. The molar conductances of $[Ni(DCCD)(H_2O)_2]Cl_2$ and $[Ni(DICD)(H_2O)_2]Cl_2 \cdot H_2O$ are 250 and 240 $Ohm^{-1} cm^2 mol^{-1}$, respectively, for 2:1 electrolytes. $[Cu_3(HBCH)(H_2O)_6]Cl_6$ is a 6:1 electrolyte exhibiting conductance of 580 $Ohm^{-1} cm^2 mol^{-1}$ [16, 47]. The magnetic susceptibility measurements indicate that the nickel(II) and copper(II) complexes have μ_{eff} of ~2.95 and ~1.80.
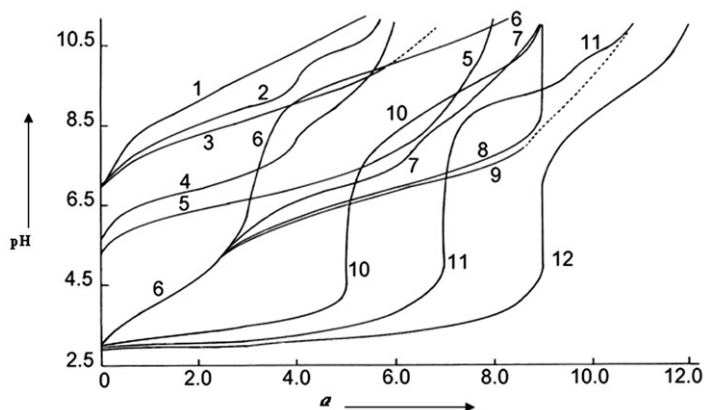
Figure 3. pH *vs. a* curves: (1) HBCH·6HCl, (2) Ni^{2+}–HBCH·6HCl, (3) 2Ni^{2+}–HBCH·6HCl, (4) Cu^{2+}–HBCH·6HCl, (5) 2Cu^{2+}–HBCH·6HCl, (6) NACT·9HCl, (7) Ni^{2+}–NACT·9HCl, (8) 2Ni^{2+}–NACT·9HCl, (9) 3Ni^{2+}–NACT·9HCl, (10) Cu^{2+}–NACT·9HCl, (11) 2Cu^{2+}–NACT·9HCl, and (12) 3Cu^{2+}–NACT·9HCl (HBCH·6HCl / NACT·9HCl = 0.0005 M, ... curve is turbidity region).

3.9. *Solution stability*

3.9.1. HBCH system. Titration curve of HBCH · 6HCl (figure 3) shows six proton–ligand equilibria. Formation of CuH$_2$A^{4+} is evident from 1:1, copper(II):HBCH titration curve which shows a steep inflection at $a = 4$ (pH ~ 8.0). A gradual color change from greenish-blue to violet below pH of inflection also supports its formation. A further increase in a (to $a = 6$) indicates existence of CuHA^{3+} and CuA^{2+}. However, the color of the mixture does not change further above pH ~ 8.0. A steep inflection at $a = 8$ also appears in the titration curve of 2:1, copper(II):ligand mixture. The color change in the mixture (greenish-blue to violet) is comparable to that of 1:1, copper(II):ligand system. Existence of species Cu$_2$A^{4+}, Cu$_2$A(OH)$^{3+}$, and Cu$_2$A(OH)$_2^{2+}$ has been inferred by the analysis of the titration curve. The corresponding equilibrium constants are reported in table 2.

NiH$_2$A^{4+} is formed at higher pH (~ 9.5) as indicated by titration curve of 1:1, nickel(II):HBCH mixture, which shows a steep inflection at $a = 4$. The species NiHA^{3+} and NiA^{2+} also exist beyond $a = 4$, but the expected color change from light green to violet is not visible due to dilution. The 2:1, nickel(II):ligand mixture turns turbid beyond pH ~ 10.0 probably due to hydrolysis of the excess metal ion which does not coordinate to the remaining two N-donors. The small ligand cavity is unable to accommodate the second nickel(II) which has tendency to form an octahedral structure.

An inflection at $a = 4$ in the titration curve of 1:1, metal:HBCH mixture indicates that metal is coordinated to four N-donors of two –NH(CH$_2$)$_3$NH– groups in the spherical cavity. The two N-donors of the third –NH(CH$_2$)$_3$NH– group are free. The four metal coordinated N-donors are expected in square-planar arrangement with equal metal–nitrogen bonds. The inflection at $a = 4$ is again possible if 2, 3, 4, and 5 metals (each coordinated to four aza donors) are accommodated in structures II, III, IV, and V, respectively. Structures II(a), III(a), IV(a), and V(a) can accommodate 2, 3, 4, and 5 metal ions, respectively, in their smaller [12]-N$_4$ cavities. But, in the nickel(II) system not more than one nickel(II) is coordinated to the macrocycle while the larger cavities of

Table 2. Equilibrium constants for nickel(II)/copper(II) complexes of HBCH and NACT (A) at 25 °C ($\mu = 0.1$ M KNO_3).

Reaction	Log K^*	
	HBCH	NACT
$H_9A^{9+} \Leftrightarrow H_8A^{8+} + H^+$	–	−3.56
$H_8A^{8+} \Leftrightarrow H_7A^{7+} + H^+$	–	−4.24
$H_7A^{7+} \Leftrightarrow H_6A^{6+} + H^+$	–	−5.02
$H_6A^{6+} \Leftrightarrow H_5A^{5+} + H^+$	−7.96	−8.35
$H_5A^{5+} \Leftrightarrow H_4A^{4+} + H^+$	−8.80	−9.42
$H_4A^{4+} \Leftrightarrow H_3A^{3+} + H^+$	−9.48	−9.85
$H_3A^{3+} \Leftrightarrow H_2A^{2+} + H^+$	−10.05	−10.26
$H_2A^{2+} \Leftrightarrow HA^+ + H^+$	−10.70	−10.77
$HA^+ \Leftrightarrow A + H^+$	−11.35	−11.30
$Ni^{2+} + H_2A^{2+} \Leftrightarrow NiH_2A^{4+}$	5.99	–
$Ni^{2+} + H_3A^{3+} \Leftrightarrow NiH_3A^{5+}$	–	11.37
$Ni^{2+} + A \Leftrightarrow NiA^{2+}$	6.93	16.32
$NiH_3A^{5+} \Leftrightarrow NiH_2A^{4+} + H^+$	–	−8.06
$NiH_2A^{4+} \Leftrightarrow NiHA^{3+} + H^+$	−10.26	−9.08
$NiHA^{3+} \Leftrightarrow NiA^{2+} + H^+$	−10.85	−10.24
$NiA^{2+} + Ni^{2+} \Leftrightarrow Ni_2A^{4+}$	–	10.91
$Cu^{2+} + H_4A^{4+} \Leftrightarrow CuH_4A^{6+}$	–	17.21
$Cu^{2+} + H_2A^{2+} \Leftrightarrow CuH_2A^{4+}$	11.81	–
$Cu^{2+} + A \Leftrightarrow CuA^{2+}$	15.41	23.27
$CuH_4A^{6+} \Leftrightarrow CuH_3A^{5+} + H^+$	–	−7.70
$CuH_3A^{5+} \Leftrightarrow CuH_2A^{4+} + H^+$	–	−8.78
$CuH_2A^{4+} \Leftrightarrow CuHA^{3+} + H^+$	−8.65	−9.48
$CuHA^{3+} \Leftrightarrow CuA^{2+} + H^+$	−9.80	−10.15
$CuH_2A^{4+} + Cu^{2+} \Leftrightarrow Cu_2H_2A^{6+}$	–	12.60
$CuA^{2+} + Cu^{2+} \Leftrightarrow Cu_2A^{4+}$	7.62	14.33
$Cu_2H_2A^{6+} \Leftrightarrow Cu_2HA^{5+} + H^+$	–	−8.68
$Cu_2HA^{5+} \Leftrightarrow Cu_2A^{4+} + H^+$	–	−9.22
$Cu_2A^{4+} + OH^- \Leftrightarrow Cu_2A(OH)^{3+}$	5.75	4.20
$Cu_2A(OH)^{3+} + OH^- \Leftrightarrow Cu_2A(OH)_2^{2+}$	4.20	3.32
$Cu_2A^{4+} + Cu^{2+} \Leftrightarrow Cu_3A^{6+}$	–	14.32
$Cu_3A^{6+} + OH^- \Leftrightarrow Cu_3A(OH)^{5+}$	–	5.80
$Cu_3A(OH)^{5+} + OH^- \Leftrightarrow Cu_3A(OH)_2^{4+}$	–	4.76
$Cu_3A(OH)_2^{4+} + OH^- \Leftrightarrow Cu_3A(OH)_3^{3+}$	–	3.90

*Values are ±0.06–0.28.

II(a), III(a), IV(a), or V(a) can accommodate two or three nickel ions. Thus, coordination of a single nickel(II) is expected in the structure of the smallest cavity such as HBCH. Hence structures II(a), III(a), IV(a), or V(a) are not acceptable.

No two –NH(CH_2)$_3$NH– groups of structure II(b) and only one pair of these groups of structure IV(b) can accommodate a metal ion through four N-donors. Therefore, II(b) and IV(b) cannot explain the inflection on the titration curve at $a = 4$. Further, there are three, four, and five vertical faces in structures III(b), IV(c), and V(b), respectively. Each vertical face consisting of 24 atoms (16 C and 8 N) can accommodate one metal involving the coordination of upper and lower edges through four N-donors. Thus, an inflection at $a = 4$ in the titration curve for these systems is possible; on account of the large cavity size a very weak metal–ligand association is expected. A vertical face ring consists of two large and two small bridges (bridge combination 7,3,7,3). Each large bridge contains 5C and 2N's while there are only three carbons in a small bridge. In addition, the complex molecule will be under strain due to less flexible structures. Further, the geometry of the resulting tri-, tetra- and penta-copper(II)

complexes of III(b), IV(c), and V(b), respectively (if formed), would not allow coordination of additional copper(II) ions (3, 4, and 5, respectively) to the free N-donors contained in the vertical edges as the atom of each vertical edge (common to two vertical face cavities) are part of a large bridge of seven atoms. But, a mononuclear copper(II) complex of HBCH favors coordination of a second copper(II) in the cavity in aqueous solution.

A tetraaza cavity formed by two $-NH(CH_2)_3NH-$ groups ([12]-N_4) in structure I (HBCH) is thus suitable to accommodate a metal ion. However, the equilibrium constant (log $K = 15.41$) for $Cu^{2+} + A \Leftrightarrow CuA^{2+}$ is low as compared to those of planar ring systems TACD ([10]-N_4, log $K = 19.34$) [14] and 1,4,7,10-tetraazacyclododecane (cyclam, [12]-N_4, log $K = 24.8$) [48]. Here, cage effect on stability constant is not exhibited due to the participation of only four N-donors in coordinate bond formation, as the geometry of the cage does not allow the remaining two nitrogens to donate their lone pair of electrons. A low stability constant value can also be expected for a non-planar ring cavity formed by the two $-NH(CH_2)_3NH-$ groups involved in bonding. In addition, the uncoordinated $-NH(CH_2)_3NH-$ group can oppose accommodation of the metal ion in the cavity by rotation through $C(1)-N(13)$ and $C(7)-N(17)$ bonds. As a result of such steric hindrance, the stability constant further decreases to a value which is lower than that reported for similar planar tetraaza ring systems. In the dimetallic copper(II) complex, the second copper(II) is expected to coordinate the ligand through only two N-donors of the third $-NH(CH_2)_3NH-$ group.

3.9.2. NACT system. The ligand titration curve (figure 3) shows a steep inflection at $a = 3$ (pH ~ 6.0), indicating coexistence of the equilibria $H_9A^{9+} \Leftrightarrow H_8A^{8+} + H^+$, $H_8A^{8+} \Leftrightarrow H_7A^{7+} + H^+$ and $H_7A^{7+} \Leftrightarrow H_6A^{6+} + H^+$ below this pH, while the remaining six proton–ligand dissociations occur at higher pH. The color of the 1:1, copper(II):NACT solution is light blue at pH ~ 3.0 with intensity increasing with increase in pH. The corresponding titration curve shows a steep inflection at $a = 5$ (pH ~ 4.3). The increase in color intensity and the inflection in the titration curve are in support of CuH_4A^{6+} formation in solution. A second inflection in the titration curve appears at the highest a value. The 2:1 or 3:1, copper(II):ligand solution is also light blue at pH ~ 3.0, but the change in color intensity follows the order $1:1 < 2:1 < 3:1$ (copper(II):ligand). Also, the 2:1 and 3:1, copper(II):NACT titration curves show steep inflections at $a = 7$ and 9 (each at pH ~ 5.0), respectively, where the formation of $Cu_2H_2A^{6+}$ and Cu_3A^{6+} are expected. The highest value of $a = 11$ in 2:1, metal:ligand system is due to dissociation of two protons from the protonated complex followed by the formation of hydroxo complexes $Cu_2A(OH)^{3+}$ and $Cu_2A(OH)_2^{2+}$. The titration curve for 3:1, copper(II):ligand system shows an additional steep inflection at $a = 12$. Coordination of 3OH$^-$ groups, one to each copper ion, is thus expected between pH ~ 7.0 and 11.0.

Each titration mixture (1:1, 2:1, or 3:1, nickel(II):NACT) system remains almost colorless due to dilution. An inflection at $a = 6$ (pH ~ 7.5) in the titration curve of the 1:1, nickel(II):NACT system indicates the formation of a protonated complex NiH_3A^{5+}. A second inflection is at $a = 9$ (pH ~ 11.0). Dissociation of three protons from NiH_3A^{5+} is expected between $a = 6$ and 9. Similarly, a very steep inflection in the titration curve of 2:1, nickel(II):ligand system is due to the formation of a dinickel(II) complex Ni_2A^{4+}. There is no coordination of OH$^-$ to Ni_2A^{4+} due to poorer complexing

of nickel(II) than copper(II). The 3:1, nickel(II):ligand titration curve slightly deviates from the curve for 2:1 system at pH ~ 8.0, and the corresponding titration mixture turns turbid beyond this pH due to the hydrolysis of excess nickel. From a comparison of 2:1 and 3:1, metal:ligand systems it appears that only two nickel(II) ions are accommodated in the spherical cavity of the macrocycle and the third nickel is free in the latter system and precipitated as $Ni(OH)_2$.

The small cavities formed by the hexaaza groups 2,5,8,10,13,16, 10,13,16,17,20,23 or 2,5,8,17,20,23 are non-planar; a high equilibrium constant ($\log K = 23.27$) for $Cu^{2+} + A \Leftrightarrow CuA^{2+}$ is expected in a square planar arrangement of a planar or similar cavity. Such arrangement of donors is possible by involvement of the aza groups 2, 5, 8 and 13 in coordination to copper in CuH_4A^{6+}. The six ring atoms 10, 11, 12, 14, 15, and 16 are expected above or below the plane of the small cavity of sixteen atoms. In addition, one of the two aza groups, 10 and 16 (both uncoordinated to copper(II) in CuH_4A^{6+}) is nonprotonated while the second is protonated. Aza groups 17, 20, and 23 are also protonated, and thus these facts explain the inflection at $a = 5$ in the pH *vs* a curve. Non-protonation of aza groups 10 or 16 is also favored by the ligand titration curve as the one aza group is completely deprotonated in the absence of metal ion at pH ~ 3.8.

The inflection at $a = 7$ in the titration curve for 2:1, copper(II):ligand system indicates that additional three protons are liberated from protonated aza groups 17, 20, and 23 due to their involvement in coordination with a second copper ion, while the first copper(II)–N(13) bond breaks to avoid crowding within the spherical cavity of the macrocycle and subsequently aza group 13 becomes protonated by accepting a proton from the medium (liberated from 17, 20, or 23). Thus, in $Cu_2H_2A^{6+}$ each copper(II) ion is coordinated to three aza donors contained in different $–NH(CH_2)_2NH(CH_2)_2NH–$ groups. Deprotonation of $Cu_2H_2A^{6+}$ to Cu_2A^{4+} and then its association to two OH^- groups, as indicated by the titration curve for 2:1, copper(II):ligand system, is also in agreement with coordination of only three N-donors to copper.

An inflection at $a = 9$ in the titration curve for 3:1, copper(II):ligand system further indicates that three copper ions are accommodated in the spherical cavity where each copper is coordinated to one $–NH(CH_2)_2NH(CH_2)_2NH–$ group through its three N-donors. Finally, the fourth coordination position of each copper(II) is occupied by OH^- by the replacement of H_2O because of high OH^- concentration, and to avoid crowding due to larger H_2O in the spherical cavity. The equilibrium constant values for $Cu_3A(OH)^{5+}$, $Cu_3A(OH)_2^{4+}$, and $Cu_3A(OH)_3^{3+}$ are higher than those reported for $Cu_2A(OH)^{3+}$ and $Cu_2A(OH)_2^{2+}$ (table 2).

Formation of a nickel(II) octahedral complex surrounded by six aza donors of the two $–NH(CH_2)_2NH(CH_2)_2NH–$ groups is expected in 1:1, nickel(II):ligand system, where the corresponding titration curve shows an inflection at $a = 6$. The aza donors 2, 8, 10, and 16 are expected in the XY plane with axial positions occupied by N(5) and N(13). In the 2:1, nickel(II):ligand system the second nickel is coordinated to only three aza donors (17, 20, and 23).

The stability constants for $Cu^{2+} + A \Leftrightarrow CuA^{2+}$ (table 2) is close to those of the copper(II) complexes of other tetraaza planar ring systems ([13]-N_4 and [15]-N_4, $\log K = 24.8$ and 24.4, respectively) [49]. The equilibrium constant ($\log K = 14.33$) for $CuA^{2+} + Cu^{2+} \Leftrightarrow Cu_2A^{4+}$ is almost comparable to that of recently reported [16] copper(II) complex of [20]-N_8 ring ($\log K = 14.59$), while each copper(II) in [20]-N_8 is coordinated to four aza donors. A high equilibrium constant value has already

been reported for $Cu_2A^{4+} + Cu^{2+} \Leftrightarrow Cu_3A^{6+}$ ($\log K = 16.69$) in the $[25]\text{-}N_{10}$ macrocycle [16].

4. Conclusion

Most of the nickel(II) tetraaza macrocyclic complexes studied earlier are diamagnetic and square planar. But, both the nickel(II) complexes of DCCD and DICD are paramagnetic and octahedral. The nickel(II) is coordinated to four aza donors in $[10]\text{-}N_4$ and $[12]\text{-}N_4$ planar cavity of the macrocycle and the axial positions are occupied by two water molecules. $[Cu_3(HBCH)(H_2O)_6]Cl_6$ is also a rare type of complex where three copper(II) ions and six water molecules are accommodated in a very small spherical cavity of 2,6,8,12,13,17-hexaazabicyclo-[5.5.5]heptadecane. Each copper(II) is bound to two aza donors of the cage and two water molecules in a square-planar environment, but none of the three planes passes through the center of the spherical cavity. Potentiometric measurements on the 1 : 1, copper(II) : NACT system show that copper(II) is coordinated to only four N-donors of the ligand which has a 3-D arrangement of nine aza groups. The arrangement of binding sites and the large spherical cavity size of the macrocycle are unsuitable to form a stable complex. But, the equilibrium constant ($\log K = 23.27$) for the reaction $Cu^{2+} + A \Leftrightarrow CuA^{2+}$ ($A = NACT$) is very high due to unique conformational change in the ligand to form a nearly planar cavity by involvement of the aza donors of positions 2, 5, 8, and 13 where copper(II) fits well.

Acknowledgements

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