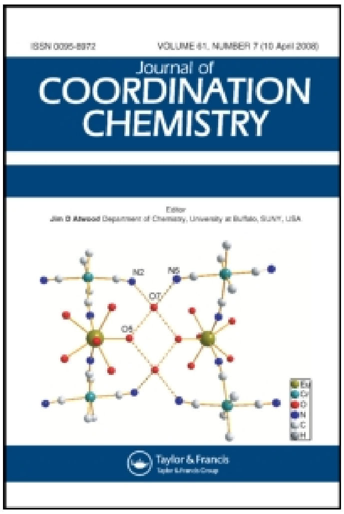

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Trinuclear copper(II) complexes of some aza macrocycles

Anurag[a]; Anil K. Pande[a]; Ram Nayan[a]
[a] Department of Chemistry, Hindu College, Moradabad - 244001, India

To cite this Article Anurag, Pande, Anil K. and Nayan, Ram(2006) 'Trinuclear copper(II) complexes of some aza macrocycles', Journal of Coordination Chemistry, 59: 17, 1963 — 1975
To link to this Article: DOI: 10.1080/00958970600737841
URL: http://dx.doi.org/10.1080/00958970600737841

Journal of Coordination Chemistry
Vol. 59, No. 17, 20 November 2006, 1963–1975

Trinuclear copper(II) complexes of some aza macrocycles

ANURAG, ANIL K. PANDE and RAM NAYAN*

Department of Chemistry, Hindu College, Moradabad – 244001, India

(*Received 25 October 2005; in final form 16 February 2006*)

The syntheses of copper(II) complexes with neutral macrocyclic ligands 1,4,7,10,12,-15,17,20,23,26,27,30-dodecaazadispiro[10·4·10·4]triacontane (DDST), 2,5,7,10,13,15,18,21,-23,26,29,32-dodecaazatricyclo[20·10·0·0^{6,17}]dotriacontane (DOCD) and 2,5,7,10,13,16,18,-21,23,26,29,32-dodecaaza-1,6,17,22-tetrachlorotricyclo[20·10·0·0^{6,17}]dotriacontane (DTTD) derived from triethylenetetramine, 1,2-diaminoethane and chlorocarbons (carbon tetrachloride, 1,l,2,2-tetrachloroethane and hexachloroethane, respectively) have been studied. Complexes $[Cu_3(DDST)]Cl_6$, $[Cu_3(DOCD)]Cl_6$ and $[Cu_3(DTTD)]Cl_6 \cdot H_2O$ and the copper ion-free ligand hydrochlorides DDST · 12HCl and DOCD · 12HCl are supported by elemental analyses, conductivity measurements and spectroscopic studies. Potentiometric equilibrium studies on DDST and DOCD hydrochlorides and their copper complexes also support the structures.

1. Introduction

Mononuclear nickel(II) and copper(II) complexes with 13-membered macrocyclic tetraza ligand 11,13-dimethyl-1,4,7,10-tetraazacyclotrideca-10,13-diene, formed *via* template condensation of triethylentetramine with acetylacetone have been reported by Cummings *et al.* [1, 2]. Recently, we extended the reaction of triethylenetetramine to other ring systems involving condensation with carbon tetrachloride, 1,1,2,2-tetrachloroethane, hexachloroethane, nickel adepate and nickel phthalate complexes [3–5] in equimolar amounts. Eleven membered ring product 11,11-dichloro-1,4,7,10-tetraazacycloundecane is generated in the refluxed mixture containing carbon tetrachloride [3]. The four aza groups of the ligand are expected to coordinate to nickel(II) or copper(II). In the 1,1,2,2-tetrachloroethane system the nickel(II) complex of the ligand 1,12-dichloro-1,4,7,10-tetraazacyclododecane has been synthesized [4]. The corresponding blue copper complex could not be isolated from the condensed equimolar mixture [5]. Further, template condensation of two moles of triethylenetetramine with one mole of 1,1,2,2-tetrachoroethane in the presence of nickel(II) yielded a dinuclear nikel(II) complex of the macrocycle 1,4,7,10,12,15,18,21-octaazabicyclo[10·10·0]docosane [4]. Similarly, the copper complex of 1,1,12,12-tetrachloro-l,4,7,10-tetraazacyclodecane could not be isolated from the hexachloroethane system [5]. In continuation, of this work our aim is to increase the number of tetraaza

---

*Corresponding author. Fax: 91-591-2440070. Email: ramnayan_2003@yahoo.co.in

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2006 Taylor & Francis
DOI: 10.1080/00958970600737841

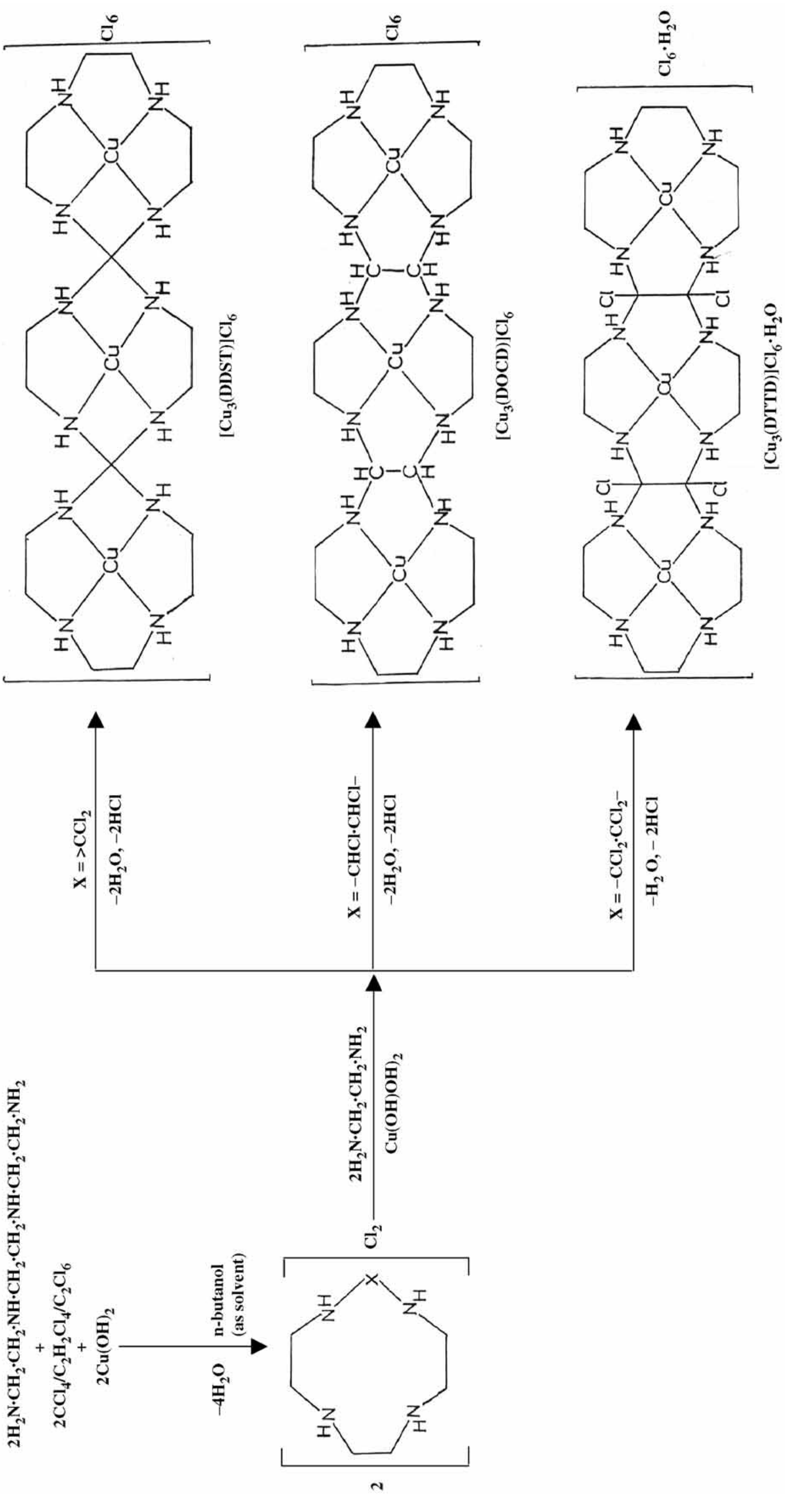

Figure 1. Reaction scheme.

rings to three. Such complexes are of importance due to their relative rarity and to study the effect of increase in ring number of the macrocycle on the stability constant of its metal complexes as a ‘cryptate effect’ in macrobicylic systems [6]. The condensed product of equimolar chlorocarbon and triethylenetetramine has been further refluxed introducing a 2 : 1 molar mixture of 1,2-diaminoethane and copper hydroxide (figure 1). Thus, three new macrocycles, 1,4,7,10,12,15,17,20,23,26,27,30-dodecaaza-dispiro[10·4·10·4]triacontane (DDST), 2,5,7,10,13,-15,18,21,23,26,29,32-dodecaaza-tricyclo[20·10·0·0^{6,17}]dotriacontane (DOCD) and 2,5,7,10,13,16,18,21,23,26,29 32-dodecaaza-1,6,17,22-tetrachlorotricyclo[20·10·0·0^{6,17}]dotriacontane (DTTD), each consisting of three rings, are generated in the carbon tetrachloride, 1,1,2,2-tetrachloroethane and hexachloroethane systems, respectively. Potentiometric equilibrium studies on the copper complexes of DDST and DOCD indicate that stability constants are enhanced due to macrocyclic effect by the presence of cyclic rings.

2. Experimental

2.1. *Chemicals and reagents*

Metal salts $Cu(NO_3)_2 \cdot 3H_2O$ (Qualigens) and KNO_3 (Loba Chemie), acids HCl and HNO_3 (Qualigens) and organic solvents CCl_4 (Qualigens) and ether (Rankem) were analytical grade chemicals. Other chemicals 1,1,2,2-tetrachloroethane, hexachloroethane (both CDH), triethylenetetramine (Fluka Chemika) and 1,2-diaminoethane (Qualigens) were commercially obtained and were used without further purification. $Cu(OH)_2$ was prepared from $Cu(NO_3)_2{\cdot}3H_2O$ using analytical grade NaOH (BDH). CO_2-free 0.1770 N NaOH, 0.02159 N HNO_3, 0.06 N HCl and 1.0 M KNO_3 solutions were prepared for potentiometric studies. Copper nitrate solution was prepared and the copper content was estimated by EDTA titration [7]. Aqueous solutions of DDST · 12HCl, DOCD·12HCl, $[Cu_3(DDST)]Cl_6$ and $[Cu_3(DOCD)]Cl_6$ were prepared by direct weighing.

2.2. *Measurements*

Elemental analyses were performed by the Central Drug Research Institute, Lucknow and the ionizable chloride ion in the samples was determined by conductometric titrations [8]. For obtaining the metal content, the complexes were decomposed [8] and the copper(II) content was determined by complexometric titration. Conductivity measurements were performed with a D.D.R. conductivity meter (type 304). Infrared spectra (FTIR) in the range 4000–350 cm^{-1} were recorded on a Shimadzu 820IPC spectrophotometer using KBr disks. ^1H NMR spectra were run on a Bruker DRX 300 (300 MHz FT) in D_2O solution using DSS as an internal standard. Mass spectra were recorded on a Jeol SX 102/DA-600 spectrometer/data system using argon/xenon (6 KV, 100 mA) as the FAB gas. The accelerating voltage was 10 KV and the spectra were recorded at room temperature. *m*-Nitrobenzyl alcohol was used as the matrix.

2.3. *Potentiometric titrations*

The mixtures (i) 0.002159 N HNO_3; (ii) 0.0005 M DDST · 12HCI or DOCD·12HCl + (i); (iii) 0.0005 copper nitrate + (ii); (iv) 0.001 M copper nitrate + (ii); (v) 0.0015 M copper nitrate + (ii) and (vi) 0.0005 M $[Cu_3(DDST)]Cl_6$ or $[Cu_3(DOCD)]Cl_6$ + 0.006 M HCl + (i) were titrated pH-metrically, at 25° and at ionic strength 0.10 M (KNO_3) using an EC 5656 pH-meter with combined electrode system. The initial volume of each mixture was kept at 50 mL. From the experimental data, titration curves (pH *vs.* moles of alkali used per mole of ligand, *a*) were plotted and analysed [9, 10] to obtain information on metal–ligand equilibria. The titration curve of mixture (vi) coincides with that of mixture (v) in each ligand system.

2.4. *Synthesis of the copper(II) complex of 1,4,7,10,12,15,17,20,23,26,27,30-dodecaazadispiro[10·4·10·4]triacontane (DDST)*

The macrocyclic complex (11,11-dichloro-1,4,7,10-tetraazacycloundecane)copper(II) chloride $[Cu(DTCU)]Cl_2$ was prepared by heating a mixture of copper hydroxide (5.00 g, 51.25 mmol), triethylenetetramine (7.49 g, 51.22 mmol) and carbon tetrachloride (7.88 g, 51.23 mmol) in 150 mL butanol as described earlier [3]. The two chloro groups of the macrocyclic molecule were allowed to condense with ethylenediamine (3.08 g, 51.25 mmol) in presence of an additional amount of copper hydroxide (2.50 g, 25.62 mmol). The stirred mixture of the latter two reactants in 50 mL butanol was added to the $[Cu(DTCU)]Cl_2$ solution and refluxed for 1 h. The colour of the mixture changed from greenish-brown to brown. The resulting mixture was cooled, stirred with 100 mL of water and filtered. The negligible amount of the blackish-brown residue was removed by filtration and the aqueous grey layer of the filtrate was separated from the non-aqueous brown layer. The aqueous solution was concentrated and chilled at 5°C. The resulting grey crystals of the product, associated with grey paste-like impurities were isolated. This impurity was removed by benzene/ether (1 : 1) treatment on filter paper as described earlier [8]. The grey crystals of the product $[Cu_3(DDST)]Cl_6$ were finally washed with ether and dried under reduced pressure, yield 2.40 g (11.26%).

2.5. *Synthesis of the copper(II) complex of 2,5,7,10,13,15,18,21,23,26,29,32-dodecaazatricyclo[20·10·0·0^{6,17}]dotriacontane (DOCD)*

A mixture of copper hydroxide (5.00 g, 51.25 mmol), triethylenetetramine (7.49 g, 51.22 mmol) and 1,1,2,2-tetrachloroethane (8.60 g, 51.24 mmol) in 150 mL butanol was refluxed for 1 h. The colour of the solution changed from blue to deep blue. Then a stirred mixture of copper hydroxide (2.50 g, 25.62 mmol) and ethylenediamine (3.08 g, 51.25 mmol) in 80 mL butanol was added to the above mixture after cooling. The resulting light blue solution was further refluxed for 3 h and 15 min. The colour of the solution immediately changed to greenish-blue after 10 min and then finally to deep blue. The macrocyclic product was extracted by 80 mL water as described above. Concentration and chilling of the bluish-violet aqueous solution below 5°C yielded sticky crystals. Fish-scale like crystals (bluish-violet) of the product $[Cu_3(DOCD)]Cl_6$ were obtained by removing blue sticky matter using benzene/ether mixture as described earlier [8].The crystals were finally washed with ether, yield 2.22 g (10.07%).

2.6. *Synthesis of the copper(II) complex of 2,5,7,10,13,16,18,21,23,26,29,32-dodecaaza-1,6,17,22-tetrachlorotricyclo[20·10·0·0^{6,17}]dotriacontane (DTTD)*

Two step condensation reaction was carried out to yield copper(II) complex of 2,5,7,10,13,16,18,21,23,26,29,32-dodecaaza-1,6,17,22-tetrachlorotricyclo[20·10·0·0^{6,17}]-dotriacontane. In the first step a mixture of copper hydroxide (4.00 g, 41.00 mmol), triethylenetetramine (6.00 g, 41.03 mmol) and hexachloroethane (9.71 g. 41.01 mmol) was refluxed in 140 mL butanol for 1h, during which the colour of the mixture changed from deep blue to brownish-yellow. The brownish-yellow colour was expected for the copper(II) complex of the macrocyclic ligand 11,11,12,12-tetrachloro-1,4,7,10-tetraazacyclododecane.

In the second step a stirred mixture of copper hydroxide (2.00 g, 20.50 mmol) and ethylenediamine (2.46 g, 40.93 mmol) in 70 mL butanol was added to the complex from the first step. The mixture was stirred and heated to reflux for 2.5 h. The brownish-blue turbid mixture changed to blackish-brown and then to blackish-green solution within 5 and 15 min, respectively. A mixture of blackish-green solution and blackish-brown precipitate was formed at the end of the reaction. The resulting mixture was cooled, and stirred with 80 mL of water. Separation of the aqueous grey solution from a negligible amount of brown residue and non-aqueous wine-red solution, concentration and then refrigeration below 5°C yielded bluish-green crude crystals of the product. The crude crystals were treated with benzene/ether (1 : 1) mixture on filter paper as usual. The filter paper absorbed greyish-blue impurities, and the green crystals of the product were then separated, washed with ether and dried, yield 2.00 g (9.60%).

Impurities associated with the products are probably the cause of low yield in each complex system. In order to increase the yield the crude product absorbed by the paper was redissolved in methanol. Evaporation of the resulting methanolic solution did not yield the complex crystal.

2.7. *Preparation of the metal-free macrocycles*

The (1,4,7,10,12,15,17,20,23,26,27,30-decaazadispiro[10·4·10·4]triacontane)copper(II) hexachloride ([Cu_3(DDST)]Cl_6 1.50 g, 1.80 mmol) and (2,5,7,10,13,16,18,21,23,26,29-32-dodecaazatricyclo[20·10·0·0^{6,17}]dotriacontane)copper(II) hexachloride ([Cu_3-(DOCD)]Cl_6 1.50 g, 1.74 mmol) were dissolved separately in 50 mL of water. Concentrated HCl (5 mL, 12 N) was added to each solution and the metal-free ligand hydrochloride aqueous solution was obtained by removing the metal ions by passing H_2S gas as described earlier [8]. Concentration and evaporation of the ligand containing aqueous solution yielded crystals of the ligand hydrochlorides DDST · 12HCl (flat, but needle shaped, light yellow) and DOCD·12HCl (flat, straw colour). The crystals were then washed with ether and dried (yield DDST · 12HCl, 1.44 g (92.91%) and DOCD · 12HCl, 1.40 g (89.77%)).

3. Results and discussion

3.1. *Synthesis*

The copper(II) complexes of the tetraaza ligands 11,11-dichloro-1,4,7,10-tetraazacycloundecane, 1,12-dichloro-l,4,7,10-tetraazacyclododecane and

1,1,12,12-tetrachloro-1,4,7,10-tetraazacyclododecane formed in equimolar mixtures of triethylenetetramine with carbon tetrachloride, 1,1,2,2-tetrachloroethane and hexachloroethane, respectively, further condense with two molecules of 1,2-diaminoethane. At the first step, the 1 : 1, copper-triethylenetetramine complex ($Cu(H_2N{\cdot}CH_2{\cdot}CH_2{\cdot}NH{\cdot}CH_2{\cdot}CH_2{\cdot}NH{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2)(OH)_2$) formed condenses with the chlorocarbon yielding a mononuclear macrocyclic copper(II) complex. The second step reaction proceeds with the formation of $Cu(H_2N{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2)_2(OH)_2$ complex in 2 : 1, 1,2-diaminoethane and copper hydroxide mixture and then its condensation with two moles of the mononuclear macrocyclic copper(II) complex formed at the first step. Thus, three new macrocycles 1,4,7,10,12,15,17,20,23,26,27,30-dodecaazadispiro[10·4·10·4]triacontane (DDST), 2,5,7,10,13,16,18,21,23,26,29,32-dodecaazatricyclo[20·10·0·0^{6,17}]dotriacontane (DOCD) and 2,5,7,10,13,16,18,21,23,26,29,32-dodecaaza-1,6,17,22-tetrachlorotricyclo[20·10·0·0^{6,17}]dotriacontane (DTTD) each with three rings are generated in the carbon tetrachloride, 1,1,2,2-tetrachloroethane and hexachloroethane systems, respectively (figure 1). All three copper(II) complexes are trinuclear and each copper ion accommodated in separate ring cavity is coordinated to four aza donors.

The formulation of the macrocyclic compounds is supported by their elemental analyses, conductivity measurements and molecular weights by mass spectrometry (table 1). The structures of the macrocycles have been inferred from spectral studies, infrared spectra and proton magnetic resonance spectra. The infrared results are strongly suggestive of the cyclic nature of the macromolecules, with absence of the band due to coordinated or free amino groups [8, 11–13].

3.2. *Infrared spectra*

The infrared spectrum of $[Cu_3(DDST)]Cl_6$ indicates the absence of bands due to the NH_2 group. A weak but very sharp band assigned to a secondary amine appears at 3123 cm^{-1}. The N–H bending mode is also seen at 1570 cm^{-1}. A strong and very sharp band at 1042 cm^{-1} may be due to ν(C–N). The vibrations for C–H asymmetric, symmetric stretching and scissoring modes are seen at the frequencies 2941 (weak), 2883 (very weak but very sharp) and 1456 cm^{-1} (medium but sharp), respectively. The ν(Cu–N) band (weak, very sharp), appears at 475 cm^{-1}. The metal-free ligand DDST is a completely condensed macrocycle. The infrared spectrum of its hydrochloride exhibits a weak but sharp band at 3200 cm^{-1} assigned to N–H stretching vibration for secondary amine. The weak bands at 2677, 2509, 2421 and 2374 cm^{-1} and a medium but very sharp band at 2052 are also associated with the amine hydrochloride group. Bands due to other functional groups, C–H asymmetric, symmetric stretching, scissoring and ν(C–N) appear at 2930, 2800, 1410 (very weak) and 1112 cm^{-1} (strong), respectively.

The infrared spectrum of $[Cu_3(DOCD)]Cl_6$ exhibits weak but very sharp bands at 2949, 2883 and 1462 cm^{-1}, assigned to C–H asymmetric, symmetric stretching and bending modes, respectively. The ν(N–H) vibration for secondary amine is seen at 3134 cm^{-1}. The N–H bending band appears as a very weak but very sharp peak at 1587 cm^{-1}. A strong but sharp band at 1119 cm^{-1} is attributed to ν(C–N). Coordination of the ligand to copper is indicated by a medium but very sharp band at 530 cm^{-1}. Many other bands may be associated with the skeletal vibration of the complex.

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

Compound	Colour (Colour at D.P.)	Yield (%) (m.p.°C)	Λ_M ($\text{ohm}^{-1}\,\text{cm}^2\,\text{mol}^{-1}$)	% Found (Calcd)					Molecular weight found (Calcd)
				C	H	N	Ni/Cu	Cl[b]	
$[Cu_3(DDST)]Cl_6$	Grey	11.26	696	25.96	5.33	20.28	22.98	25.52	–
$C_{18}H_{44}Cl_6Cu_3N_{12}$	(brown)	(210)[d]		(25.98)	(5.34)	(21.21)	(22.91)	(25.56)	
$DDST \cdot 12HCl$	Light yellow	92.21	–	24.98	6.52	19.38	–	49.01	866.0
$C_{18}H_{56}Cl_{12}N_{12}$	(light black)	(238)[d]		(24.96)	(6.53)	(19.41)	–	(49.11)	(866.3)
$[Cu_3(DOCD)]Cl_6$	Bluish-violet	10.07	736	27.98	5.62	19.50	22.22	–	–
$C_{20}H_{48}Cl_6Cu_3N_{12}$	(brown)[a]	(230)		(27.93)	(5.64)	(19.55)	(22.16)	–	
$DOCD \cdot 12HCl$	Straw	89.77	–	26.80	6.76	18.77	–	47.66	894.0
$C_{20}H_{60}Cl_{12}N_{12}$	(brown)	(260)[d]		(26.86)	(6.78)	(18.80)	–	(47.57)	(894.3)
$[Cu_3(DTTD)]Cl_6 \cdot H_2O$	Green	9.60	680	23.66	4.58	16.58	18.72	20.90	–
$C_{20}H_{46}Cl_6Cu_3N_{12}O$	(black)[a]	(160)[d]		(23.46)	(4.57)	(16.55)	(18.76)	(20.94)	

[a] Black at 265°C, [b] ionizable chloride ion, [d] decomposition.

In the infrared spectrum of ligand hydrochloride very weak bands attributed to N–H stretching and bending modes are at 3190 and 1568 cm^{-1}, respectively. The ν(C–N) vibration is observed as a weak band at 1200 cm^{-1}. Many weak or very weak bands associated with the amine hydrochloride groups are seen at 2730, 2700, 2620, 2502, 2430, 2374, 2287 and 2058 cm^{-1}. A strong but broad band for C–H stretching appears at 3000–2800 cm^{-1}. The corresponding scissoring vibration (very weak but broad) is observed at 1410 cm^{-1}.

Presence of water in $[Cu_3(DTTD)]Cl_6 \cdot H_2O$ is evident by the medium bands of 3231 and 1659 cm^{-1}. These bands are assigned to O–H stretching and bending [14]. The compound exhibits very sharp vibrations at 3130 (very weak) and 1570 cm^{-1} (medium) attributed to ν(N–H) and δ(N–H), respectively, for the secondary amine groups. A very weak peak for ν(C–N) is seen at 1092 cm^{-1}. The ν(Cu–N) band (weak but very sharp) is at 472 cm^{-1}. Bands at 2930 (weak), 2883 (very weak but sharp) and 1458 cm^{-1} (medium but very sharp) are due to C–H asymmetric, symmetric stretching and δ(C–H) modes, respectively.

3.3. *Comparison with related systems*

In the copper complex of DDST the two side rings ([11]-N_4) have bridge combinations (2,2,2,1) similar to that in macrocycle, 1,4,7,10,12,15,18,21-octaazaspiro[10·10]heneicosane (OASH) or 11,11-dichloro-1,4,7,10-tetraazacycloundecane (DTCU) reported earlier [3, 5] where each metal ion is coordinated to four aza groups. The size of the middle ring, because of its bridge combination 2,1,2,1 is slightly reduced ([10]-N_4). Probably due to this reduction in size of the middle ring the Cu–N bond order in DDST complex is not much greater than the Ni–N bond order in the nickel-OASH complex as indicated by ν(Ni–N) vibration frequency (470 cm^{-1}). Further, the greater Cu–N bond order in DDST complex than in DTCU complex, as indicated by the ν(Cu–N) vibration frequencies (475 and 440 cm^{-1}, respectively) in their copper complexes is due to absence of an inductive effect in DDST complex. The two Cl-atoms of DTCU reduce the Cu–N bond order in its copper complex.

The ring cavities in DOCD and DTTD macrocycles are identical in size where each ring ([12]-N_4) has a 2,2,2,2 bridge combination. As expected the Cu–N bond order in DTTD complex is lower than that in DOCD complex because of electron-withdrawing effect by four Cl-atoms in DTTD. A comparison of ν(Cu–N) vibration frequency of copper complex of DOCD (530 cm^{-1}) with that of DDST shows that the copper is strongly coordinated to DOCD as compared to DDST. Hence, it is expected that the copper fits more comfortably in larger cavities of DOCD. Recently, in the study of nickel complexes of some tetraaza macrocycles [l5], we reported that a larger ([12]-N_4) ring (bridge combination-2,2,2,2) has greater complexing tendency than a smaller ([10]-N_4) ring (bridge combination-2,1,2,1).

3.4. *^{1}H NMR and mass spectra*

A sharp peak in the ^{1}H NMR spectrum of the DOCD hydrochloride at 4.72 ppm is expected for NH_2^+ protons. Another signal of a complex multiplet with many peaks centered at 3.54 ppm is expected for the sum of the methylene and methyne protons. Further, the ^{1}H NMR spectrum of the DOCD complex with copper(II) is consistent with the spectrum of the ligand, which shows N–H signals at 4.84, and many complex multiplets, expected for remaining protons, centered at 3.54 ppm.

The ^{1}H NMR spectrum of the DDST ligand hydrochloride exhibits a broad singlet at 4.84 ppm and a multiplet in the region 3.82–3.34 ppm. These signals are assigned to NH_2^+ and CH_2 proton resonances, respectively. In the corresponding copper(II) complex spectrum a broad singlet at 4.71 ppm may be due to NH protons. A very complex multiplet with many peaks in the 3.70–2.01 ppm region is expected for the CH_2 protons of the complex.

The highest mass peaks in the spectrum of DDST · 12HCl and DOCD·12HCl (by FABMS) are at m/z values close to their molecular ions (table 1). These peaks are very weak and are comparable to those of many earlier reported aza macrocycles [13].

3.5. *Solubility, conductivity and other data*

In view of their ionic nature the complexes and the ligand hydrochlorides DDST · 12HCl and DOCD · 12HCl are highly soluble in water. Also, they are generally soluble in many other polar solvents like methanol, ethanol, DMF, DMSO, etc. The molecular conductivity and the number of ionizable chloride ions recorded in table 1, support their ionic nature. The molar conductance values determined for the complexes are consistent with a 6 : 1 electrolyte. The copper complexes of DTTD, DDST and DOCD are green, grey and bluish-violet, respectively. The colours of ligand hydrochlorides are: DOCD·12HCl, straw colour and DDST · 12HCl, light yellow. Table 1 shows that the compounds are thermally stable.

3.6. *Solution stability*

Existence of nine proton-ligand equilibria between pH 5.0 and 11.0 (table 2) is shown by the titration curves of the hydrochlorides of DDST (figure 2) and DOCD. The remaining three protons of each ligand do not dissociate under the experimental pH condition. Formation of CuH_8A^{10+}, $Cu_2H_4A^{8+}$ and Cu_3A^{6+} in solution is evident from the titration curves of 1 : 1, 1 : 2 and 1 : 3 metal–igand systems, which show inflections at $a = 4$, 8 and 12, respectively. A gradual colour change from greenish-blue to violet, in each titration mixture containing copper ion, below the pH of inflection also supports their formation. The colour of the mixtures does not change further above this pH. Six and five protons from the protonated complex CuH_8A^{10+} of DDST and DOCD systems, respectively, and two protons from $Cu_2H_4A^{8+}$ of each system further dissociate up to pH 11.0. The corresponding equilibrium constants are reported in table 2.

Formation of CuH_8A^{10+} is expected from the interaction of copper(II) ion and the four NH_2^+ groups with lowest pK values. From a comparison of proton dissociations from the ligand hydrochloride and from its copper complex CuH_8A^{10+} it is expected that the NH_2^+ groups of the ligand hydrochlorides with pK_5^H, pK_6^H, pK_7^H and pK_8^H, correspond to the uncoordinated NH_2^+ groups of the complex CuH_8A^{10+} with pK'_1, pK'_2, pK'_3 and pK'_4, respectively. After formation of CuH_8A^{10+} there is large decrease in pK values of these groups ($pK_5^H - pK'_1 = 2.60$ and 2.66, $pK_6^H - pK'_2 = 2.95$ and 2.56, $pK_7^H - pK'_3 = 2.71$ and 2.09 and $pK_8^H - pK'_4 = 1.62$ and 0.65 for DDST and DOCD systems, respectively). Hence, these groups may be associated with a

Table 2. Equilibrium constants for copper(II) complexes of DDST and DOCD (25°C, $\mu = 0.1$ M (KNO3)).

	[a]Log K	
Reaction	DDST system	DOCD system
$H_{12}A^{12+} \overset{K_1^H}{\rightleftharpoons} H_{11}A^{11+} + H^+$	−6.15	−6.42
$H_{11}A^{11+} \overset{K_2^H}{\rightleftharpoons} H_{10}A^{10+} + H^+$	−6.75	−6.95
$H_{10}A^{10+} \overset{K_3^H}{\rightleftharpoons} H_9A^{9+} + H^+$	−7.28	−7.40
$H_9A^{9+} \overset{K_4^H}{\rightleftharpoons} H_8A^{8+} + H^+$	−7.67	−7.90
$H_8A^{8+} \overset{K_5^H}{\rightleftharpoons} H_7A^{7+} + H^+$	−8.40	−8.80
$H_7A^{7+} \overset{K_6^H}{\rightleftharpoons} H_6A^{6+} + H^+$	−9.45	−9.60
$H_6A^{6+} \overset{K_7^H}{\rightleftharpoons} H_5A^{5+} + H^+$	−10.06	−10.15
$H_5A^{5+} \overset{K_8^H}{\rightleftharpoons} H_4A^{4+} + H^+$	−10.50	−10.55
$H_4A^{4+} \overset{K_9^H}{\rightleftharpoons} H_3A^{3+} + H^+$	−10.85	−10.85
$Cu^{2+} + H_8A^{8+} \overset{K'}{\rightleftharpoons} CuH_8A^{10+}$	13.45	13.77
$CuH_8A^{10+} \overset{K_1'}{\rightleftharpoons} CuH_7A^{9+} + H^+$	−5.80	−6.14
$CuH_7A^{9+} \overset{K_2'}{\rightleftharpoons} CuH_6A^{8+} + H^+$	−6.50	−7.04
$CuH_6A^{8+} \overset{K_3'}{\rightleftharpoons} CuH_5A^{7+} + H^+$	−7.35	−8.06
$CuH_5A^{7+} \overset{K_4'}{\rightleftharpoons} CuH_4A^{6+} + H^+$	−8.88	−9.90
$CuH_4A^{6+} \overset{K_5'}{\rightleftharpoons} CuH_3A^{5+} + H^+$	−10.02	−10.56
$CuH_3A^{5+} \overset{K_6'}{\rightleftharpoons} CuH_2A^{4+} + H^+$	−10.65	–
$Cu^{2+} + CuH_4A^{6+} \overset{K''}{\rightleftharpoons} Cu_2H_4A^{8+}$	11.28	13.09
$Cu_2H_4A^{8+} \overset{K_1''}{\rightleftharpoons} Cu_2H_3A^{7+} + H^+$	−6.80	−6.90
$Cu_2H_3A^{7+} \overset{K_2''}{\rightleftharpoons} Cu_2H_2A^{6+} + H^+$	−9.15	−9.20
$Cu^{2+} + Cu_2H_2A^{8+} \overset{K'''}{\rightleftharpoons} Cu_3A^{6+} + 2H^+$	−8.48	−8.06
$Cu^{2+} + A \overset{K_1}{\rightleftharpoons} CuA^{2+}$	24.16*	22.02*
$Cu^{2+} + CuA^{2+} \overset{K_2}{\rightleftharpoons} Cu_2A^{4+}$	16.00*	16.75*

[a] Values are ±0.04–0.12, *approximate value.

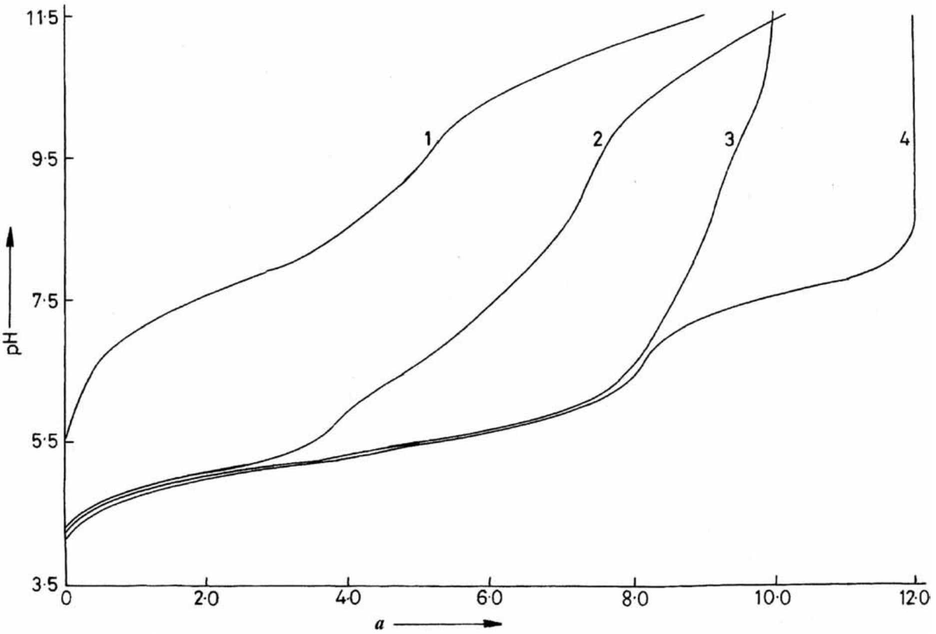

Figure 2. pH *vs.* *a* curves: (1) DDST · 12HCl, (2) Cu^{2+} – DDST · 12HCl, (3) $2Cu^{2+}$ – DDST · 12HCl and (4) $3Cu^{2+}$ – DDST · 12HCl (DDST · 12HCl = 0.0005 M).

second ring adjacent to the first ring (metal coordinated ring). On the other hand, the difference between pK_9^H and pK'_5 is comparatively low (0.83 in the DDST system and 0.29, DOCD system), and therefore, the related NH_2^+ group appears away form the metal coordinated ring. Similarly, in 2 : 1 metal–ligand system liberation of no protons from $Cu_2H_2A^{6+}$ species indicates that the corresponding two uncoordinated groups are also in the third ring. Thus, in CuH_8A the single copper ion is accommodated in one of the two side rings. The additional copper ion in Cu_2H_4A is accommodated in the middle ring (figure 2).

High equilibrium constant values (K′ or K″) for copper complexes of DDST or DOCD reported in table 2 are due to the macrocyclic effect. The smaller ring size of DDST ([11]-N_4 or [10]-N_4) than those of DOCD ([12]-N_4) are probably responsible for comparatively low K′ or K″ values in DDST complexes. Deviation in K″ values is more significant as the second copper ion is accommodated in the middle ring where the ring size difference in DDST and DOCD is largest. The exact equilibrium constant value for the reaction involving non-protonated species CuA^{2+} ($Cu^{2+} + A \overset{K_1}{\rightleftharpoons} CuA^{2+}$) and the values for many other reactions, $H_3A^{3+} \overset{K_{10}^H}{\rightleftharpoons} H_2A^{2+} + H^+$, $H_2A^{2+} \overset{K_{11}^H}{\rightleftharpoons} HA^+ + H^+$ and $HA^+ \overset{K_{12}^H}{\rightleftharpoons} A + H^+$, $CuH_3A^{5+} \overset{K'_6}{\rightleftharpoons} CuH_2A^{4+} + H^+$, (DOCD system), $Cu_2H_2A^{4+} \rightleftharpoons CuHA^{3+} + H^+$ and $CuHA^{3+} \overset{K_0^1}{\rightleftharpoons} CuA^{2+} + H^+$ could not be evaluated from the experimental data as the few NH_2^+ protons of the third ring do not dissociate under the experimental condition. But, the expression $K_1 = K'K'_1K'_2K'_8/K_5^HK_6^HK_{12}^H$ can be simplified for obtaining and approximate K_1 value. As discussed above, the pK values of the NH_2^+ groups related to the third ring of the metal-free macromolecule and its copper complex CuH_8A^{10+} are expected very close to each other (i.e. $pK^H_{10} \sim pK'_6$, $pK^H_{11} \sim pK'_7$ and $pK^H_{12} \sim pK'_8$). Thus, $K_1 = K'K'_1K'_2K'_3K'_4K'_5/K^H_5K^H_6$-$K^H_7K^H_8K^H_9$ was used to evaluate and approximate K_1 value. The K_1 value for DOCD systems (table 2) is very close to the equilibrium constant value earlier reported [16] for copper complex of the smallest aza macrocycle, 1,4,7,10-tetraazacyclododecane consisting [12]-N_4 ring ($K_1 = 10^{24.8}$). The unexpectedly high approximate value for DDST system is due to comparatively high $pK^H_7 - pK'_3$ and $pK^H_8 - pK'_4$ values, which may be associated with the spiral structure of the ligand. An error associated with each constant used for K_1 calculation can also affect the value.

The equilibria $Cu_2H_2A^{6+} \overset{K''_3}{\rightleftharpoons} Cu_2HA^{5+} + H^+$ and $Cu_2HA^{5+} \overset{K''_4}{\rightleftharpoons} Cu_2A^{4+} + H^+$ involving the two aza protons of the third ring do not exist under the experimental condition. But, these protons are displaced after coordination of all four aza groups to the third copper ion. Further, from a comparison of $pK'_5 - pK''_1 = 3.22$ and $pK'_6 - pK''_2 = 1.50$ values (table 2) the pK''_3 and pK''_4 are expected close to pK'_7 and pK'_8, respectively, as described in the 1 : 1 system. Thus an approximate value for equilibrium $Cu^{2+} + CuA^{2+} \overset{K_2}{\rightleftharpoons} Cu_2A^{4+}$ can be evaluated by modifying the equation $K_2 = K''K''_1K''_2K''_3K''_4/K'_5K'_6K'_7K'_8$ to $K_2 = K''K''_1K''_2/K'_5K'_6$. The value for DOCD system ($K_2 = K''K''_1/K'_5$) is less accurate and lower than the correct value.

In view of the basic nature of the four aza groups associated with the third ring a comparatively high value of stability constant for the equilibrium $Cu^{2+} + Cu_2A^{4+} \overset{K_3}{\rightleftharpoons} Cu_3A^{6+}$ is expected. However, the K_3 could not be obtained from the experimental data due to non-existence of Cu_2A^{4+} species in solution below pH 11.0. Since, the reactions $Cu_2H_2A^{6+} \overset{K''_3}{\rightleftharpoons} Cu_2HA^{5+} + H^+$ or $Cu_2HA^{5+} \overset{K''_4}{\rightleftharpoons} CuA^{2+} + H^+$, in 2 : 1 metal–ligand system, exist above pH 11.0, the corresponding equilibrium constant (K''_3 and K''_4) values may be considered much smaller than 10^{-11}. Thus, for a 10^{-12} assumed value of K''_3 or K''_4, K_3 ($K_3 = K'''/K''_3K''_4$) is expected about 10^{16}.

Acknowledgement

The authors are thankful to the Regional Sophisticated Instrumentation Centre, Central Drug Research Institute, Lucknow for recording the IR spectra, mass spectra and ^1H NMR spectra and determining the microanalyses.

References

[1] S.C. Cummings, R.E. Sievers. *J. Amer. Chem. Soc.*, **92**, 215 (1970); *Inorg. Chem.*, **9**, 1131 (1970).
[2] S.C. Cummings. *Inorg. Chem.*, **11**, 475 (1972).
[3] Anurag, R. Nayan. *J. Ind. Chem. Soc.*, **82**, 485 (2005).
[4] M. Singh, R. Nayan. *Ind. J. Chem.*, **35A**, 239 (1996).
[5] Anurag. Studies on some macrocyclic ligands and their metal complexes. PhD thesis, Rohilkhand Univ. (2002).
[6] J.M. Lehn, J.P. Sauvage. *J. Amer. Chem. Soc.*, **97**, 6700 (1975).

[7] J. Bassett, R.C. Denny, G.H. Jeffery, J. Mendham. *Vogel's Text Book of Quantitative Inorganic Analysis*, 4th Edn, Longman Group Ltd., London (1978).
[8] M. Singh, R. Nayan. *Synth. React. Inorg. Met.-Org. Chem.*, **27**, 619 (1997).
[9] R. Nayan, A.K. Dey. *Ind. J. Chem.*, **14A**, 892 (1976).
[10] R. Nayan. *J. Inorg. Nucl. Chem.*, **43**(12), 3283 (1981).
[11] S.C. Jakels, K. Farmery, E.K. Barefield, N.J. Rose, D.H. Bush. *Inorg. Chem.*, **11**(12), 2893 (1972).
[12] M.S. Holtman, S.C. Cummings. *Inorg. Chem.*, **15**(3), 660 (1976).
[13] M. Singh, R. Nayan. *Synth. React. Inorg. Met.-Org. Chem.*, **28**(1), 87 (1998).
[14] K. Burger. *Coordination Chemistry, Experimental Methods*, p. 52, Butterworths, London (1973).
[15] M. Singh, Anurag, R. Nayan. *Synth. React. Inorg. Met.-Org. Chem.*, **30**(9), 1703 (2000).
[16] R.M. Izatt, J.S. Bradshaw, S.A. Nielsen, J.D. Lamb, J.J. Christensen, D. Sen. *Chem. Rev.*, **85**(4), 271 (1985).