Inorganic Chemistry Communications 13 (2010) 1156–1159

Contents lists available at ScienceDirect

Inorganic Chemistry Communications

journal homepage: www.elsevier.com/locate/inoche

Synthesis and characterization of dinuclear copper(II) complexes, [Cu$_2$([20]-DCHDC)(L$_a$)$_2$] (L$_a$ = N$_3^-$, NCS$^-$ or S$_2$O$_3^{2-}$) with tetraazadiphenol macrocyclic ligand having cyclohexane rings

Jong Chul Byun [a],*, Nam Ho Lee [a], Dae Hun Mun [b], Ki Min Park [c],*

[a] Department of Chemistry, College of Natural Sciences, Jeju National University, Jeju 690-756, Republic of Korea
[b] Research Institute for Basic Sciences, Jeju National University, Jeju 690-756, Republic of Korea
[c] Department of Chemistry and Research Institute of Natural Science, Gyeongsang National University, Jinju 660-701, Republic of Korea

ARTICLE INFO

Article history:
Received 19 April 2010
Accepted 13 June 2010
Available online 19 June 2010

Keywords:
Tetraazadiphenolic macrocycle
Dinuclear copper(II) complex
Square pyramidal geometry
Monodentate azido ligand

ABSTRACT

The chiral dinuclear tetraazadiphenol macrocyclic copper(II) complexes [Cu$_2$([20]-DCHDC)(L$_a$)$_2$] {H$_2$[20]-DCHDC = 14,29-dimethyl-3,10,18,25-tetraazapentacyclo-[25,3,1,0^{4,9},1^{12,16},0^{19,24}]ditriacontane-2,10,12,14,16(32),17,27(31),28,30-decane-31,32-diol; L$_a$ = N$_3^-$ (**II**), NCS$^-$ (**IV**) or S$_2$O$_3^{2-}$ (**V**)} has been synthesized and structurally characterized by elemental analysis, conductance, electronic and IR spectra as well as FAB-MS method. Crystal structure of [Cu$_2$([20]-DCHDC)(N$_3$)$_2$]·2CH$_3$OH (**III**) determined by X-ray crystallography reveal the two square pyramidal copper centers bridged by the two phenoxide oxygen atoms, with large Cu–O–Cu angles {100.88(10)°}.

Schiff base Robson-type macrocycles containing two bridging phenol groups have been widely used to synthesize homo- and hetero-dinuclear complexes [1]. Most investigations of these metal complexes are an outgrowth of bioinorganic chemistry and enzymatic catalysis research [2]. Typically, Robson-type macrocyclic complexes like tetraazadiphenol macrocyclic transition metal complexes have been derived from the template condensation of achiral diamines such as ethylenediamine or diethylenetriamine and 2-hydroxy-5-methyl-benzene-1, 3-dicarbaldehyde [1]. However, the use of chiral diamines such as 1*R*,2*R*-diaminocyclohexane, 1*R*,2*R*-diphenylethylenediamine, and *R*-1,1-binaphthalenyl-2,2-diamine in the construction of chiral Schiff base Robson-type macrocycles has received only limited study [3]. Recently, we have reported the first mononuclear Ni(II) complex with tetraazadiphenolic macrocycle bearing chiral precursor 1,2-diaminocyclohexane rings in the lateral and/or head units [4]. Our primary interest in these compounds arises from the combination of the synthetic and structural chemistry of chiral macrocycles and how they differ from their achiral counterparts.

The charged ligands like azide, nitrite, thiocyanate and thiosulfate are a versatile ligand which can bind transition metal ions in a variable manner giving rise to terminal, end-on bridging and end-to-end bridging modes described elsewhere [5]. The versatility of the azide, nitrite, thiocyanate and thiosulfate anions not only enriches the stereochemistry of the metal ions but also their spectroscopic and magnetic properties.

In our continuous efforts to assemble transition metal ion(II) polyaza and oxaaza Schiff base macrocyclic complexes containing the anionic ligands, we hope to expand the system of the azido, thiocyanato and thiosulfato homodinuclear complexes of Cu(II) with tetraazadiphenol macrocycle. With an aim to synthesize [Cu$_2$([20]-DCHDC)(N$_3$)$_2$]·6H$_2$O (**II**), [Cu$_2$([20]-DCHDC)(NCS)$_2$]·H$_2$O (**IV**) and [Cu$_2$([20]-DCHDC)(μ-S$_2$O$_3$)] (**V**) {H$_2$[20]-DCHDC = 14,29-dimethyl-3,10,18,25-tetraazapentacyclo-[25,3,1,0^{4,9},1^{12,16},0^{19,24}] ditriacontane-2,10,12,14,16(32),17,27(31),28,30-decane-31,32-diol}, we have carried out the preparation of the dinucleating compartmental O$_2$N$_4$-donor macrocyclic complex, [Cu$_2$([20]-DCHDC)Cl$_2$]·H$_2$O (**I**) possessing two trans replaceable sites being occupied by two chloride ions (Scheme 1).

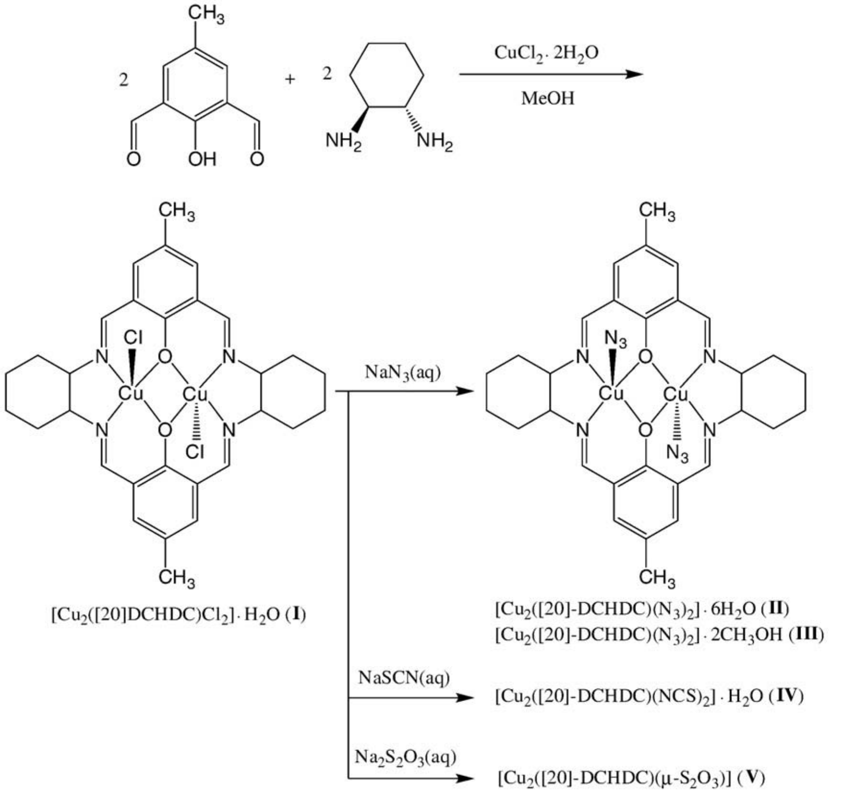
Reaction of complex **I**, recently reported by our group [4,6] and sodium azide in water provided the dark brown precipitates analyzing as complex **II**. Crystallization of complex **II** on slow evaporation of solvent methanol gave stable monoclinic crystals, [Cu$_2$([20]-DCHDC)(N$_3$)$_2$]·2CH$_3$OH (**III**) suitable for X-ray crystallography. Dinuclear copper(II) complexes, **IV** and **V** were prepared by following a procedure similar to that described in complex **II**, using aqueous solution of sodium thiocyanate and sodium thiosulfate instead of sodium azide, respectively.

The molar conductivity measurement of complexes **II**, **IV** and **V** exhibits 30–50 Ω^{-1} cm^2 mol^{-1} (DMSO), typical of non-electrolytic nature in this solvent. The visible spectra of complexes **II**, **IV** and **V** show a characteristic band near 560 nm. In general typical Cu(II)

---

* Corresponding author. Tel.: +82 64 754 3544; fax: +82 64 756 3561.
E-mail addresses: jchbyun@cheju.ac.kr (J.C. Byun), kmpark@gnu.ac.kr (K.M. Park).

1387-7003/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.inoche.2010.06.035



Scheme 1. Synthetic route of the dinuclear tetraazadiphenol macrocyclic copper(II) complexes.

complexes of square pyramidal(SP) or distorted SP geometries exhibit a band in the 550–650 nm range [7].

The formation of binuclear Cu(II) complex, inferable from elemental analysis [8], molar conductance and electronic absorption spectra of **II**, **IV** and **V**, is evidenced by characteristic IR absorption bands and mass spectrum. For complexes **II**, **IV** and **V**, strong evidence that aldehyde groups had been completely converted into Schiff base residues was provided by the disappearance of the aldehydic C=O stretching band at 1680 cm^{-1} and the appearance of a strong band at 1630 ± 5 cm^{-1} assigned to ν(C=N) stretching band [9]. The bands that appear near 3020–2930 cm^{-1} and 1550 cm^{-1} are due to C–H and aromatic ring C=C stretching vibrations, respectively. The sharp absorption bands near 1240 cm^{-1} are attributed to phenolic C–O vibration. In the spectra of complexes **II**, **IV** and **V**, Cu–N(macrocycle) vibrations occur at almost 503 cm^{-1} [9(a, b)].

The IR spectrum of complex **II** shows absorptions around 3460 and 3340 cm^{-1} which may possibly arises from a ν(O–H) of the lattice water. The IR spectrum of the anionic ligands in complex **II** appears at 2030 and 1320 cm^{-1} corresponding to the asymmetric and symmetric –NNN stretching vibrations, respectively, which is consistent with the crystal structure [9(a),10].

A band corresponding to ν(O–H) of complex **IV** is observed around 3460 cm^{-1}. The absorption bands at 2070 and 890 cm^{-1} observed in complex **IV** may reasonably correspond to ν(CN) and ν(CS) of the *N*-bonded NCS^-, respectively [9(a),10(a, c),11].

The absorption bands in the 1240–1200 and 1020–1010 cm^{-1} regions observed in complex **V** are associated with the asymmetric and symmetric stretching modes of bidentate thiosulfato ligand, respectively. Other vibrational modes are found in deformation bands at 629 and 598 cm^{-1} regions, and S–S stretching band of $S_2O_3^{2-}$ at 532 cm^{-1} [9(b), 12]. We reported a single crystal structure of the complex, $[Ni_2([22]\text{-HMTADO})(\mu(O,S)\text{-}S_2O_3)]$, where [22]-HMTADO is the dinuclear oxaazamacro-cyclic ligand [12].

The significant ions observed in the FAB mass spectrum of complexes **II**, **IV** and **V** include $[Cu_2(L_{bac})]^+$, $[Cu([20]\text{-DCHDC})]^+$ and $[Cu_2([20]\text{-DCHDC})]^+$ at *m/z* 526, 545 and 608, respectively. On the contrary the acyclic fragment ion ($[Cu_2(L_{bac})]^+$) of complexes **II**, **IV** and **V** was detected with significant abundance, macrocycle H_2[20]-DCHDC or H_2[22]-HMTADO leaves intact in the complexes $[Ni(H_2[20]\text{-DCHDC})](ClO_4)_2$, $[Ni_2([22]\text{-HMTADO})(CN)_2]\cdot 0.5H_2O$, $[Ni_2([22]\text{-HMTADO})(\mu\text{-}O_2N)(NO_2)(OH_2)]$, $[Cu_2([22]\text{-HMTADO})(H_2O)_4]Cl_2\cdot 10H_2O$ [1(c),4]. We observe that in these complexes macrocycle is more stable than that of complexes **II**, **IV** and **V** under the conditions of this analysis. The mass spectrum of complexes **II**, **IV** and **V** shows a major fragment centered around *m/z* 650, 666 and 704, which are ascribed to the $[Cu_2([20]\text{-DCHDC})(N_3)]^+$, $[Cu_2([20]\text{-DCHDC})(NCS)]^+$ and $[Cu_2([20]\text{-DCHDC})(SO_4)]^+$, respectively, a result that strongly supports the presence of dinuclear active sites in the macrocyclic complexes. The cluster of peaks of mass one or two greater or less around *m/z* 704, which is due to a $[Cu_2([20]\text{-DCHDC})(SO_4)]^+$ of complex **V** accounts for the slight ambiguities in making assignments. In the experimental conditions employed, thiosulfate ion is transformed into sulfate ion by oxidation reaction and sulfur–sulfur bond fission of thiosulfato ligand [13]. Mass procedure and IR spectrum in addition to Reference [12] indicate that the two metal centers captured inside one oxaazamacro-cyclic ligand are linked by the thiosulfate sulfur and oxygen.

Crystal **III** crystallizes in the monoclinic space group $P2_1/c$ with $a = 6.9849(5)$ Å, $b = 19.6663(13)$ Å, $c = 12.0317(8)$ Å, and $\beta = 97.1770(10)°$ [14]. Structural determination (Fig. 1) reveals that complex **III** possesses a neutral dinuclear structure, where each Cu(II) has a five-coordinated square pyramidal geometry with the N_2O_2-donor dinucleating macrocycle [20]-DCHDC adopting a tetradentate ligand about the central metal and the remaining one coordination site being occupied by a monodentate azido ligand. The macrocyclic complex adopts an essentially flat structure with the two square