Inorganica Chimica Acta 395 (2013) 160–168

Contents lists available at SciVerse ScienceDirect

Inorganica Chimica Acta

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

Synthesis of non-symmetrically substituted tetraimine macrocyclic complexes of copper(II) and nickel(II)

Mateusz Woźny, Iwona Mames, Bohdan Korybut-Daszkiewicz *

Institute of Organic Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland

ARTICLE INFO

Article history:
Received 23 July 2012
Received in revised form 25 October 2012
Accepted 30 October 2012
Available online 8 November 2012

Keywords:
Copper complexes
Nickel complexes
Macrocyclic ligands
Ligand design
Schiff bases

ABSTRACT

The non-symmetrically functionalized neutral 6,13-substituted-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraene complexes of copper(II) and nickel(II) were synthesized by mesylation of symmetric diol derivatives in neat, anhydrous pyridine at 0 °C. The products of monomesylation were used to obtain macrocyclic copper(II) and nickel(II) complexes substituted with bulky terminal group on one end and thiol functional group on the other. Linear arrangements of two or three macrocyclic units terminally blocked with bulky tris(*p*-*tert*-butylphenyl)(4-phenoxy)methane substituents were obtained from monomesylated intermediates. Free ligands obtained by demetallation reaction of neutral copper(II) tetraazamacrocyclic complexes were used for the synthesis of nickel(II) analogs.

1. Introduction

The first macrocyclic tetraimine complexes, often referred to as Jäger macrocycles, were synthesized by template condensation of bis(β-ketoaldimine)nickel(II) or copper(II) complexes with ethylene- or 1,3-propylenediamine [1–3]. Jäger cyclization procedure – with the application of triformylmethane as the starting material – leads to the formation of complexes substituted only with two formyl groups in *meso* positions [4,5]. The carbonyl groups in *meso* positions of neutral macrocyclic tetraimine complexes can be *O*-methylated transforming them into reactive enol–ether di-cations. The appended methoxy substituents are readily replaced by amino residues leading to the formation of the cationic cyclidene complexes (Scheme 1A). Bridged with α,ω-diamines, macrobicylic (lacunar) cyclidene complexes of iron(II) and cobalt(II) were extensively studied by Busch et al. as reversible dioxygen carriers [6].

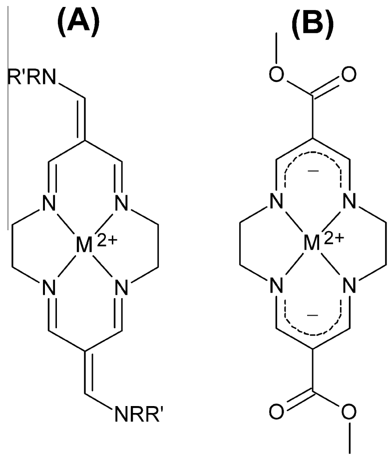
Macrocyclic tetraimines form stable complexes with nickel(II) and copper(II) ions and can be reversibly oxidized to 3+ oxidation state. The double bonds in planar β-diimine 6-membered chelate rings are delocalized. Therefore, these rings can be recognized through π–π donor–acceptor interactions. In our group we have explored synthesis and properties of dinuclear, bismacrocyclic cyclidenes composed of planar 14-membered dicationic units, and utilized their π-acceptor properties [7]. For example tetracationic rings composed of two joined π-acceptor complex units were used to construct a [2]catenane with a dibenzocrown ether as a π-donor element surrounding half of the bismacrocyclic heterodinuclear cationic complex. Change in redox state of the adjacent metal center induced the translocation of the crown to the oxidized one and now more favorable π-acceptor, what was experimentally observed with electroanalytical techniques [8].

Neutral Jäger complexes are characterized by higher electron density than π-acceptor cationic ones [9], and can be treated as potential π-donors. In order to investigate chemical, electrochemical and supramolecular properties of this type of complexes, we have used tetraimine macrocyclic complexes substituted with ester groups in *meso* positions (Scheme 1B). The synthesis of the appropriate 14-membered ligand – 6,13-bis(methoxycarbonyl)-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraene was reported by Takamura [10]. The 15- and 16-membered analogs were synthesized following the template Jäger synthetic strategy [2,3] from 2-formyl-3-hydroxypropenoic methyl ester and appropriate diamines [11]. Diester complexes are synthetically useful, because it is possible to carry out a transesterification reactions of the starting methyl esters with various diols. Reaction with diols introduces two terminal hydroxyl groups (e.g., **1Ni** and **1Cu** shown in Scheme 2) which later can be transformed in to another functional groups. In particular, we have shown that dithiol derivatives are suitable for self-assembly into electroactive monolayers (SAM) on gold surface [12,13]. Chemisorption occurred spontaneously at room temperature, and does not required any special conditions, while SAMs were electrochemically stable, and the redox process was reversible. As expected molecules build into SAMs were able to interact with π-electron deficient molecules in solution, what proves that neutral tetraazamacrocyclic complexes exhibit π-donor character [14].

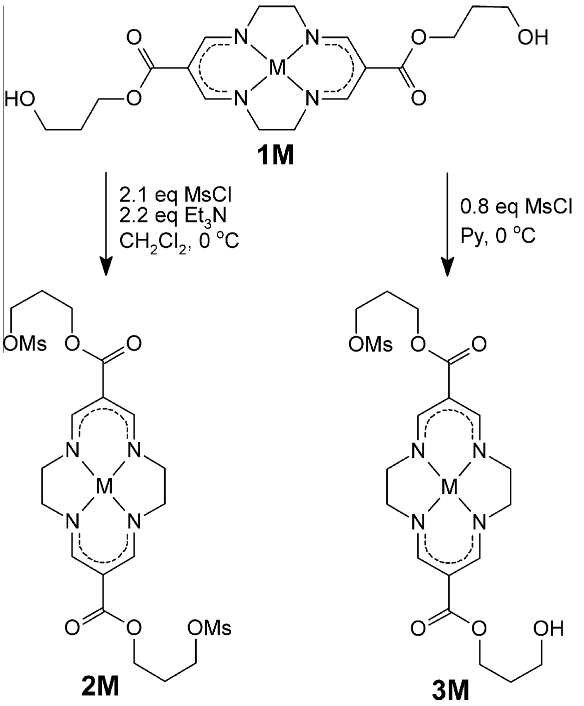
---

* Corresponding author. Tel.: +48 22 3432035; fax: +48 22 632 66 81.
E-mail address: bkd@icho.edu.pl (B. Korybut-Daszkiewicz).

0020-1693/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.ica.2012.10.027



Scheme 1.



Scheme 2.

The macrocyclic diol diesters **1Ni** and **1Cu** (Scheme 2) are substituted with two chemically identical hydroxyl groups as centers of further chemical modification. Therefore, the aim of this work was finding of a method for the efficient monofunctionalization at the one of two terminal hydroxyl groups. Such synthetic step is required if one wants to synthesize derivatives containing different structural fragments on two opposite ester groups, including larger molecules containing 'linearly' arranged macrocyclic units of neutral complexes.

2. Experimental

2.1. Materials

All chemicals and solvents used were obtained from commercial sources and were used as received without further purification. Macrocyclic complexes **1Ni, 1Cu, 2Ni, 2Cu** [12], **11Ni** [15] and tris(p-*tert*-butylphenyl)(4-hydroxyphenyl)methane **(4)** [16] were obtained according to previously described procedures.

2.2. Measurements

ESI or FD mass spectra were measured with a Mariner Perceptive Biosystem and Walters Micromass GCT Premier mass spectrometers, respectively. The ^{1}H and ^{13}C NMR spectra were obtained with Varian Mercury 400, Varian VNMRS 500 and Varian VNMRS 600 spectrometers. In cases of ambiguous assignment of observed NMR shifts to appropriate ^{1}H or ^{13}C nuclei, ^{1}H–^{13}C HSQC correlations spectra were applied. Signals are reported in ppm relative to the residual solvent signal, $\delta(CHCl_3) = 7.26$ ppm. In NMR data descriptions C and H atoms constituting tritylphenol structural motif are referred as follows: C_a ($O–C_{sp2}$); C_b and H_b (C_{sp2}–H in *ortho* position to ether bond), C_c and H_c (C_{sp2}–H in *meta* position to ether bond), C_d (C_{sp2} in *para* position to ether bond), C_e (central quaternary C_{sp3} atom of the tritylphenol), C_f (C_{sp2} in *para* position to *tert*-Bu group), C_g and H_g (C_{sp2}–H in *meta* position to *tert*-Bu group), C_h and H_h (C_{sp2}–H in *ortho* position to *tert*-Bu group), C_i (C_{sp2}-*tert*-Bu group), C_j (quaternary C_{sp3} atom in *tert*-Bu), C_k and H_k (C_{sp3}–H in methyl groups).

2.3. Synthesis

$1^{2+}(PF_6^-)_2$ from 1Cu: 106.1 mg (0.233 mmol) of **1Cu** was dissolved in the mixture of 10 ml MeOH and 5 ml CH_2Cl_2. Hydrogen chloride was bubbled through the solution until its color changed to yellow completely. Solvents were rotary evaporated, and 5 ml of water was added, to dissolve the salt, followed by addition of 150 mg of NH_4PF_6 in 0.5 ml of water. Di(hexafluorophosphate) of protonated ligand $\mathbf{1^{2+}}$ precipitates immediately. This salt was filtered, washed with copious amounts of water, portion of MeOH, Et_2O, and then dried in vacuo. Yield: 144.8 mg (90%). *Anal.* Calc. for $C_{18}H_{30}F_{12}N_4O_6P_2$ (688.4): C, 31.41; H, 4.39; N, 8.14. Found: C, 31.52; H, 4.36; N, 8.20%. ESI MS (MeCN, *m*/*z*): 199.1 $[C_{18}H_{30}N_4O_6]^{2+}$, 397.2 $[C_{18}H_{29}N_4O_6]^{+}$, 543.2 $[C_{18}H_{30}N_4O_6{\cdot}PF_6]^{+}$. ^{1}H NMR (CD_3CN, 600 MHz, δ (ppm)): 1.99 p (4H, *J* = 5.3 Hz, CH_2CH_2OH), 3.51 m (4H, axial protons in NCH_2CH_2N), 3.83 t (4H, *J* = 5.1 Hz, CH_2OH), 3.91 m (4H, equatorial protons in NCH_2CH_2N), 4.44 t (4H, *J* = 5.6 Hz, $CH_2(CH_2)_2OH$), 7.54 d (4H, *J* = 15.4 Hz, CH = N), 10.31 br (4H, NH). ^{13}C NMR (CD_3CN, 150 MHz, δ (ppm)): 30.2 (CH_2CH_2OH), 51.1 (NCH_2), 61.0 (CH_2OH), 65.8 ($CH_2(CH_2)_2OH$), 95.3 ($C_{sp2}C(O)$), 165.2 (C = O), 166.0 (CH = N). ^{1}H–^{15}N HMBC ($CDCl_3$, 600 MHz) reveals correlations between CH = N nitrogen (-236.1 ppm), and equatorial protons in NCH_2CH_2N (3.91 ppm).

1Ni from $1^{2+}(PF_6^-)_2$: 95.5 mg of the hexafluorophosphate salt of $\mathbf{1^{2+}}$ (0.139 mmol) was dissolved in 5.0 ml of MeCN. A solution of 41.5 mg of nickel(II) acetate tetrahydrate (1.2 eq) in 4.0 ml of MeOH was added, followed by 79.5 µl of Et_3N (4.1 eq). After 2 h the solution was evaporated to dryness. Orange solid was dissolved in $2{:}1_{vol}$ CH_2Cl_2:MeOH, and the product separated from the mixture by simple silica gel chromatography with 8% MeOH in CH_2Cl_2 as an eluent. **1Ni** fraction was concentrated, and the product was precipitated upon addition of Et_2O, and dried. Yield: 54.8 mg (87%). The product is in all respects identical to **1Ni** obtained from previously described standard synthesis.

3Ni: 2.027 g of anhydrous diol **1Ni** (4.473 mmol) was dissolved in 50 ml of dry pyridine upon heating. The solution was chilled to 0 °C and 276.9 µl of mesyl chloride (0.8 eq) was added slowly to the stirred clear solution. The reaction was carried out for 45 min at 0 °C, then allowed to reach room temperature, and left for 30 min. Then, the majority of solvent was vacuum evaporated, and 40 ml of diethyl ether was added to the oily remnants. The precipitate was filtered off, rinsed with diethyl ether (3 × 25 ml), and dried. Orange solid was suspended in 5 ml of CH_2Cl_2. This