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

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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].

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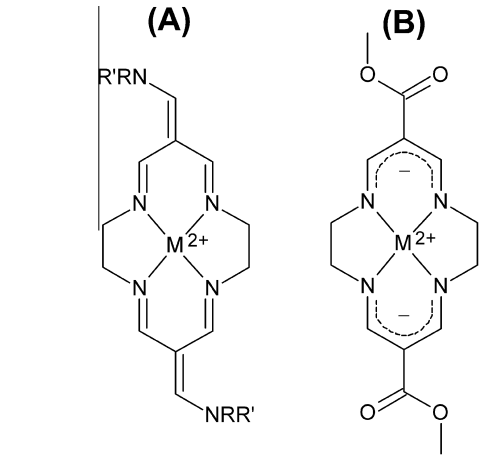
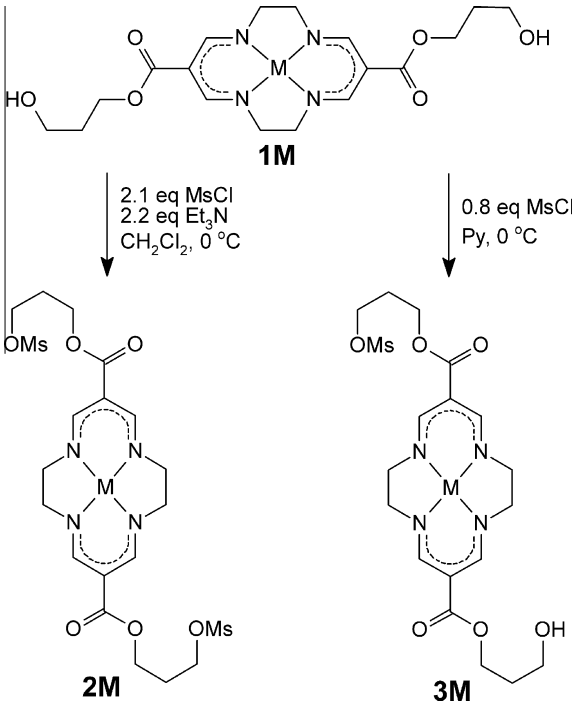


Scheme 1.



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_2-OH), 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

suspension was applied to chromatographic column and purified by dry column vacuum chromatography method, using 60 g of aluminum oxide 150 (type T) for TLC as an adsorbent. Gradient elution starting from 100% CH_2Cl_2, and ending with 5% MeOH in CH_2Cl_2 allowed to collect fractions of **2Ni**, **3Ni**, and **1Ni** subsequently. Fractions were concentrated on rotary evaporator, and diluted with hexane. Precipitates formed immediately, were filtered off, rinsed with hexane and dried in vacuo. Yield of **2Ni** by-product was 9%, also 30% of **1Ni** was recovered. Yield of the main product **3Ni**: 1.412 g (56% versus **1Ni**, that is 70% versus MsCl). *Anal.* Calc. for $C_{19}H_{28}N_4NiO_8S$ (531.2): C, 42.96; H, 5.31; N, 10.55. Found: C, 43.00; H, 5.51; N, 10.62%. TOF MS FD$^+$ (CH_2Cl_2, *m*/*z*): 530.1 [$C_{19}H_{28}N_4NiO_8S$]$^+$. ^{1}H NMR ($CDCl_3$, 400 MHz, δ (ppm)): 1.88 p (2H, *J* = 5.9 Hz, C*H*$_2$CH$_2$OH), 2.13 p (2H, *J* = 6.1 Hz, C*H*$_2$CH$_2$OMs), 3.03 s (3H, SO_2CH_3), 3.40 bs (8H, NCH_2), 3.66 t (2H, *J* = 5.8 Hz, C*H*$_2$OH), 4.29 t (2H, *J* = 5.8 Hz, CH_2OMs), 4.35 t (4H, C(O)OCH_2), 7.81 s and 7.82 s (4H, CH = N). ^{13}C NMR ($CDCl_3$, 100 MHz, δ (ppm)): 28.9 (*C*H$_2$-CH$_2$OMs), 32.6 (*C*H$_2$CH$_2$OH), 37.6 (SO_2CH_3), 58.90, 58.95, 59.19, 59.94 and 60.26 (two NCH_2, two C(O)O*C*H$_2$, CH_2OH), 67.0 (CH$_2$-OMs), 98.3 and 98.9 (two macrocycle C_{sp2}C(O)), 154.9 and 155.2 (two CH=N), 169.0 and 169.6 (two C=O).

3Cu: This compound was synthesized from diol **1Cu** following the above procedure for **3Ni**. Yield 55% versus **1Cu**, that is 69% versus MsCl. *Anal.* Calc. for $C_{19}H_{28}CuN_4O_8S$ H_2O (554.1): C, 41.19; H, 5.46; N, 10.11. Found: C, 41.22; H, 5.36; N, 10.20%. TOF MS FD$^+$ (CH_2Cl_2, *m*/*z*): 535.1 [$C_{19}H_{28}CuN_4O_8S$]$^+$.

5Ni from 2Ni: 0.462 g of dimesylate complex **2Ni** (0.759 mmol), and 0.803 g tris(*p*-tertbutylphenyl)(4-hydroxyfenyl)methane (2.1 eq) were dissolved in 50 ml of anhydrous DMF. 1.483 g of anhydrous Cs_2CO_3 (6.0 eq) and about 1 g of 3 Å MS were added. The resulting mixture was stirred for 3 days at room temperature. Solids were filtered off, and filtrate was poured into 150 ml of water. Immediately formed precipitate was filtered off, washed with water (3 × 50 ml) and methanol (25 ml), followed by dissolution in CH_2Cl_2, and chromatographic purification (DCVC column with Silica Gel 60 PF_{254} TLC-grade, eluted with CH_2Cl_2). The first orange-colored fraction was collected, and the solvent partially removed by vacuum evaporation. The product **5Ni** was precipitated with methanol, and dried in vacuo. Yield: 0.769 g (71%). Anal. Calc. for $C_{92}H_{110}N_4NiO_6$ (1426.6): C, 77.45; H, 7.77; N, 3.93. Found: C, 77.50; H, 7.82; N, 3.82%. TOF MS FD$^+$ (CH_2Cl_2, *m*/*z*): 1424.8 [$C_{92}H_{110}N_4NiO_6$]$^+$. ^{1}H NMR ($CDCl_3$, 500 MHz, δ (ppm)): 1.30 s (54H, H_k), 2.14 p (4H, *J* = 6.3 Hz, $CH_2CH_2CH_2$), 3.34 s (8H, NCH_2), 4.04 t (4H, *J* = 6.2 Hz, CH_2OAr), 4.33 t (4H, *J* = 6.1 Hz, C(O)OCH_2), 6.77 m (4H, H_b), 7.07 m (16H, H_c and H_g), 7.23 m (12H, H_h), 7.79 s (4H, CH=N). ^{13}C NMR ($CDCl_3$, 125 MHz, δ (ppm)): 29.2 ($CH_2CH_2CH_2$), 31.4 (C_k), 34.3 (C_j), 58.7 (NCH_2), 60.3 (C(O)OCH_2), 63.0 (C_e), 64.6 (CH_2OAr), 98.3 (macrocycle C_{sp2}C(O)), 113.0 (C_b), 124.0 (C_h), 130.7 (C_g), 132.2 (C_c), 139.7 (C_d), 144.1 (C_f), 148.3 (C_i), 154.9 (CH=N), 156.6 (C_a), 167.7 (C=O). NMR signals assignment supported by ^{1}H–^{13}C HSQC correlation spectra ($CDCl_3$, 600/150 MHz).

5Cu: This compound was synthesized from dimesylate **2Cu** following the above procedure for **5Ni**. Yield 69%. *Anal.* Calc. for $C_{92}H_{110}CuN_4O_6$ H_2O (1449.5): C, 76.24; H, 7.79; N, 3.86. Found: C, 76.14; H, 7.75; N, 3.67%. TOF MS FD$^+$ (CH_2Cl_2, *m*/*z*): 1429.9 [$C_{92}H_{110}CuN_4O_6$]$^+$.

5: 145.9 mg of **5Cu** (0.102 mmol) was dissolved in 20 ml CH_2Cl_2 and 5 ml MeOH mixture. HCl gas was bubbled through the solution until the color was changed from pink to yellow and precipitate has formed. Solvents were evaporated to dryness, and resulting solid was washed in 25 ml of water for 3 h until complete decolorization. The chloride salt was then filtrated, and washed with copious amounts of water. After drying in vacuo the product was added to the solution of 29.1 µl of triethylamine (2.05 eq) in 3 ml of CH_2Cl_2. The solution of neutralized ligand **5** was then poured on short silica gel column and eluted with CH_2Cl_2. First colorless fraction was collected and precipitated by addition of MeOH and evaporation of CH_2Cl_2. The precipitate was filtered, washed with MeOH, Et_2O and dried in vacuo. Overall yield: 96.4 mg (69%). *Anal.* Calc. for $C_{92}H_{112}N_4O_6{\cdot}H_2O$ (1387.9): C, 79.61; H, 8.28; N, 4.04. Found: C, 79.57; H, 8.25; N, 3.85%. TOF MS FD$^+$ (CH_2Cl_2, *m*/*z*): 1368.7 [$C_{92}H_{112}N_4O_6$]$^+$. ^{1}H NMR ($CDCl_3$, 500 MHz, δ (ppm)): 1.30 s (54H, H_k), 2.14 p (4H, *J* = 6.2 Hz, $CH_2CH_2CH_2$), 3.55 s (8H, NCH_2), 4.05 t (4H, *J* = 6.2 Hz, CH_2OAr), 4.33 t (4H, *J* = 6.2 Hz, C(O)OCH_2), 6.77 m (4H, H_b), 7.08 m (16H, H_c and H_g), 7.22 m (12H, H_h), 8.27 s (4H, CH=N), 12.57 s (2H, NH). ^{13}C NMR ($CDCl_3$, 125 MHz, δ (ppm)): 29.1 (CH_2-*C*H$_2$CH$_2$), 31.4 (C_k), 34.3 (C_j), 53.5 (NCH_2), 60.4 (C(O)OCH_2), 63.0 (C_e), 64.6 (CH_2OAr), 94.9 (macrocycle C_{sp2}C(O)), 112.9 (C_b), 124.0 (C_h), 130.7 (C_g), 132.2 (C_c), 139.7 (C_d), 144.1 (C_f), 148.3 (C_i), 156.6 (C_a), 157.8 br (CH=N), 168.0 (C=O). NMR signals assignment supported by ^{1}H–^{13}C HSQC correlation spectra ($CDCl_3$, 500/125 MHz).

5Ni from 5: 62.3 mg of **5** (0.045 mmol) was dissolved in 4 ml of CH_2Cl_2. A solution of 13.4 mg of nickel(II) acetate tetrahydrate (1.2 eq) in 1.0 ml MeOH was added, followed by 13.2 µl of Et_3N (2.1 eq). After 2 h the solution was evaporated to dryness. Orange solid was dissolved in CH_2Cl_2 and the product was separated chromatographically on silica gel column, with 1% MeOH in CH_2Cl_2 as an eluent. **5Ni** fraction was concentrated, and the product was precipitated upon addition of MeOH, filtrated, washed with MeOH, Et_2O and dried in vacuo. Yield: 55.4 mg (86%). The product is in all respects identical to **5Ni** obtained from **2Ni** as described above.

6Ni: 1.315 g of monomesylate complex **3Ni** (2.475 mmol), and 1.250 g tris(*p*-tertbutylphenyl)(4-hydroxyfenyl)methane (1.0 eq) were dissolved in 60 ml of anhydrous DMF. 3.230 g of anhydrous Cs_2CO_3 (4.0 eq) and about 1.5 g of molecular sieves 3 Å were added. The resulting mixture was stirred for 3 days at room temperature. Solids were filtered off, and filtrate was poured into 150 ml of water. Precipitate, which forms immediately, was filtered off, washed with water (3 × 50 ml), and dried. Orange-colored filtrate was extracted with 2 × 20 ml of CH_2Cl_2. The crude product was dissolved in the organic phase obtained from extraction. The resulting solution was then washed with 3 × 200 ml H_2O, 1 × 100 ml of saturated KCl solution, and dried with $MgSO_4$. After evaporation of the solvent the crude product was purified using DCVC method (Merck, Silica Gel 60 PF_{254} for TLC), with 2% MeOH in CH_2Cl_2 as an eluent. The first major orange-colored fraction is collected. The product was precipitated from concentrated solution with hexane, and dried in vacuo. Yield: 1.489 g (64%). *Anal.* Calc. for $C_{55}H_{68}N_4NiO_6$ (939.9): C, 70.29; H, 7.29; N, 5.96. Found: C, 70.55; H, 7.23; N, 5.76%. TOF MS FD$^+$ (CH_2Cl_2, *m*/*z*): 938.4 [$C_{55}H_{68}N_4NiO_6$]$^+$. ^{1}H NMR ($CDCl_3$, 600 MHz, δ (ppm)): 1.29 s (27H, H_k), 1.86 p (2H, *J* = 5.9 Hz, C*H*$_2$CH$_2$OH), 2.13 p (2H, *J* = 6,2 Hz, C*H*$_2$CH$_2$OAr), 3.35 s (8H, NCH_2), 3.64 t br (2H, C*H*$_2$OH), 4.03 t (2H, *J* = 6.1 Hz, CH_2OAr), 4.32 m (4H, C(O)OCH_2), 6.75 m (2H, H_b), 7.06 m (8H, H_c and H_g), 7.21 m (6H, H_h), 7.78 s (2H, CH=N on the side of bulky end group), 7.80 s (2H, CH=N on the side of OH end group). ^{13}C NMR ($CDCl_3$, 150 MHz, δ (ppm)): 29.1 (*C*H$_2$CH$_2$OAr), 31.4 (C_k), 32.5 (*C*H$_2$CH$_2$OH), 34.3 (C_j), 58.70, 58.77, 58.83 and 59.78 (two NCH_2, *C*H$_2$CH$_2$CH$_2$OH), 60.4 (*C*H$_2$(CH$_2$)$_2$OAr), 63.0 (C_e), 64.6 (CH_2OAr), 98.3 and 98.9 (two C_{sp2}C(O) in macrocycle), 112.9 (C_b), 124.0 (C_h), 130.7 (C_g), 132.3 (C_c), 139.6 (C_d), 144.1 (C_f), 148.3 (C_i), 154.9 br (CH=N), 156.6 (C_a), 167.7 and 168.6 (two C=O).

6Cu: This compound was synthesized from monomesylate **3Cu** following the above procedure for **6Ni**. Yield 61%. *Anal.* Calc. for $C_{55}H_{68}CuN_4O_6$ H_2O (962.7): C, 68.62; H, 7.33; N, 5.82. Found: C, 68.71; H, 7.33; N, 5.80%. TOF MS FD$^+$ (CH_2Cl_2, *m*/*z*): 943.3 [$C_{55}H_{68}CuN_4O_6$]$^+$.

7Ni: The solution of 1.315 g of alcohol **6Ni** (1.400 mmol) in 150 ml of dry CH_2Cl_2 was cooled to 0 °C. Two-hundred and thirty-five microliters of triethylamine (1.2 eq) and 120 µl of mesyl chloride (1.1 eq) were added. The reaction was carried out at 0 °C for 2 h, than allowed to reach room temperature. The solvent

was rotary evaporated, remnants dissolved in small volume of CH_2Cl_2 and purified chromatographically on neutral alumina column with 0.5% MeOH in CH_2Cl_2 as an eluent. The main fraction was concentrated, and product precipitated upon addition of methanol. Monomesylate **7Ni** was then filtered and dried in vacuo. Yield: 1.257 g (88%). *Anal.* Calc. for $C_{56}H_{70}N_4NiO_8S\ H_2O$ (1036.0): C, 64.93; H, 7.00; N, 5.41. Found: C, 65.00; H, 7.12; N, 5.39%. TOF MS FD$^+$ (CH_2Cl_2, *m*/*z*): 1016.4 [$C_{56}H_{70}N_4NiO_8S$]$^+$. ^{1}H NMR ($CDCl_3$, 400 MHz, δ (ppm)): 1.30 s (27H, H_k), 2.13 m (4H, $CH_2CH_2CH_2$), 3.01 s (3H, SO_2CH_3), 3.35 bs (8H, NCH_2), 4.04 t (2H, *J* = 6.2 Hz, CH_2OAr), 4.29 t (2H, *J* = 6.0 Hz, CH_2OMs), 4.34 m (4H, $C(O)OCH_2$), 6.76 m (2H, H_b), 7.07 m (8H, H_c and H_g), 7.23 m (6H, H_h), 7.79 bs (4H, CH = N). ^{13}C NMR ($CDCl_3$, 100 MHz, δ (ppm)): 28.9 (CH_2CH_2OMs), 29.2 (CH_2CH_2OAr), 31.5 (C_k), 35.7 (C_j), 37.6 (SO_2CH_3), 58.8, 58.9, 60.4 (two NCH_2, $CH_2(CH_2)_2OAr$), 63.1 (C_e), 64.6 (CH_2OAr), 67.0 (CH_2OMs), 98.3 br (two C_{sp2}C(O) in macrocycle), 113.0 (C_b), 124.1 (C_h), 130.8 (C_g), 132.3 (C_c), 139.7 (C_d), 144.2 (C_f), 148.4 (C_i), 155.1 br (two CH = N), 156.7 (C_a), 167.79 and 167.82 (two C = O).

7Cu: This compound was synthesized from **6Cu** following the procedure described for **7Ni**. Yield 81%. *Anal.* Calc. for $C_{56}H_{70}CuN_4O_8S\ H_2O$ (1039.4): C, 64.62; H, 6.97; N, 5.38. Found: C, 64.51; H, 7.03; N, 5.39%. TOF MS FD$^+$ (CH_2Cl_2, *m*/*z*): 1021.4 [$C_{56}H_{70}N_4NiO_8S$]$^+$.

8Ni: The monomesylate **7Ni** (1.100 g, 1.081 mmol) and thiourea (0.411 g, 5 eq) were dissolved in 150 ml of DMF. The reaction was carried out at 50 °C for 24 h, after which no substrate was observed on TLC plates. DMF was partially removed on rotary evaporator and 300 ml of water was added to the solution. The immediately formed precipitate of isothiouronium salt was filtered, washed with 3 × 50 ml H_2O, 50 ml MeOH, and suspended in 300 ml of cold water, without further purification. A solution of 15 g NaOH in 50 ml H_2O was then added dropwise, and the resulting mixture was stirred under inert atmosphere for 5 h. The mixture was cooled in the fridge, and about 32 ml of hydrochloric acid was added dropwise, until neutral pH was reached. The precipitate was filtered off, washed with copious amounts of water, followed by a portion of MeOH, and dried in vacuo. The crude product thus obtained was dissolved in CH_2Cl_2 and purified chromatographically (TLC-grade Silica Gel 60 PF_{254}; 1% MeOH in CH_2Cl_2 as an eluent). The first main orange-colored fraction was collected, and the solvent partially removed by vacuum evaporation. The product precipitated upon addition of Et_2O was filtered and dried in vacuo. Yield: 0.494 g (47.8%). *Anal.* Calc. for $C_{55}H_{68}N_4NiO_5S\ H_2O$ (973.9): C, 67.83; H, 7.24; N, 5.75. Found: C, 67.91; H, 7.29; N, 5.66%. TOF MS FD$^+$ (CH_2Cl_2, *m*/*z*): 954.4 [$C_{55}H_{68}N_4NiO_5S$]$^+$. ^{1}H NMR ($CDCl_3$, 400 MHz, δ (ppm)): 1.30 s (27H, H_k), 2.07 p (2H, *J* = 6.8 Hz, CH_2CH_2SH), 2.14 p (2H, *J* = 6.2 Hz, CH_2CH_2OAr), 2.77 t (2H, *J* = 7.2 Hz, CH_2SH), 3.36 s (8H, NCH_2), 4.04 t (2H, *J* = 6.2 Hz, CH_2OAr), 4.25 t (2H, *J* = 6.2 Hz, $CH_2(CH_2)_2SH$), 4.33 t (2H, *J* = 6.2 Hz, $CH_2(CH_2)_2OAr$), 6.76 m (2H, H_b), 7.08 m (8H, H_c and H_g), 7.23 m (6H, H_h), 7.79 s br (4H, two CH=N). ^{13}C NMR ($CDCl_3$, 100 MHz, δ (ppm)): 29.0 (CH_2CH_2SH), 29.3 (CH_2CH_2OAr), 31.5 (C_k), 34.4 (C_j), 35.68 and 35.71 (two $CH_2CH_2CH_2$), 58.87, 58.91, 61.011, 60.499 and 61.844 (two NCH_2, two $C(O)OCH_2$, CH_2SH), 63.2 (C_e), 64.7 (CH_2OAr), 98.3 and 98.4 (two C_{sp2}C(O) in macrocycle), 113.1 (C_b), 124.2 (C_h), 130.8 (C_g), 132.4 (C_c), 139.8 (C_d), 144.3 (C_f), 148.4 (C_i), 155.0 br (CH=N), 156.8 (C_a), 167.78 and 167.84 (two C=O).

8Cu: this compound was synthesized from **7Cu** following the procedure described above for **8Ni**. Yield 37%. *Anal.* Calc. for $C_{55}H_{68}CuN_4O_5S\ H_2O$ (978.8): C, 67.49; H, 7.21; N, 5.72. Found: C, 67.55; H, 7.30; N, 5.61%. TOF MS FD$^+$ (CH_2Cl_2, *m*/*z*): 959.4 [$C_{55}H_{68}CuN_4O_5S$]$^+$.

9Ni$_2$: 0.541 g of 3,3′-dithiodipropionic acid (2.575 mmol) was suspended in 5 ml of freshly distilled, anhydrous CH_2Cl_2. A drop of dry DMF was added, followed by 0.66 ml of oxalyl chloride (3 eq). The mixture was left for 1.5 h under inert atmosphere until it clarified and no gas formation was longer observed. The solution was evaporated to dryness and kept in vacuum for another 0.5 h to remove remnants of $(COCl)_2$. The solution of 0.726 g of alcohol **6Ni** (0.3 eq) and 0.538 ml of anhydrous Et_3N (1.5 eq) in 10 ml of dry CH_2Cl_2 containing about 0.5 g of molecular sieves 3 Å, was prepared and cooled to 0 °C. Already obtained pale-yellow oil of 3,3′-dithiodipropionic acid dichloride was dissolved in 5 ml of dry CH_2Cl_2 and added dropwise during 3 h to the solution of **6Ni**. The reaction mixture was then stirred for another 0.5 h and 3 ml of MeOH were added. After 15 min molecular sieves were filtered off, and the solution was evaporated to dryness. The crude mixture was dissolved in CH_2Cl_2 and purified chromatographically (TLC-grade Silica Gel 60 PF_{254}; CH_2Cl_2 followed by 1% MeOH in CH_2Cl_2 as eluents). Second, major orange-colored fraction was collected and concentrated. The product was precipitated upon addition of methanol, filtered off, dissolved in CH_2Cl_2 once more and precipitated upon addition of hexane, filtered and dried in vacuo. Yield: 0.499 g (56%). *Anal.* Calc. for $C_{116}H_{142}N_8Ni_2O_{14}S_2\ H_2O$ (2072.0): C, 67.24; H, 7.00; N, 5.41. Found: C, 67.23; H, 6.97; N, 5.46%. TOF MS FD$^+$ (CH_2Cl_2, *m*/*z*): 2050.9 [$C_{116}H_{142}N_8Ni_2O_{14}S_2$]$^+$. ^{1}H NMR ($CDCl_3$, 500 MHz, δ (ppm)): 1.30 s (54H, H_k), 2.02 p (4H, *J* = 6.3 Hz, $CH_2CH_2OC(O)(CH_2)_2S$), 2.14 p (4H, *J* = 6.2 Hz, CH_2CH_2OAr), 2.74 t (4H, *J* = 7.2 Hz, $C(O)CH_2$), 2.93 t (4H, *J* = 7.1 Hz, SCH_2), 3.36 s br (16H, NCH_2), 4.04 t (4H, *J* = 6.2 Hz, CH_2OAr), 4.21 t (4H, *J* = 6.4 Hz, $CH_2OC(O)(CH_2)_2S$), 4.23 t (4H, *J* = 6.3 Hz, C_{sp2}–$C(O)OCH_2(CH_2)_2OC(O)$), 4.33 t (4H, *J* = 6.2 Hz, $C(O)OCH_2(CH_2)_2OAr$), 6.76 m (4H, H_b), 7.07 m (16H, H_c and H_g), 7.23 m (12H, H_h), 7.79 s br (8H, CH = N). ^{13}C NMR ($CDCl_3$, 125 MHz, δ (ppm)): 28.4 ($CH_2CH_2OC(O)CH_2$), 29.2 (CH_2CH_2OAr), 31.4 (C_k), 33.1 (SCH_2), 34.1 ($C(O)CH_2$), 34.3 (C_j), 58.7 and 58.8 (NCH_2), 59.8 ($CH_2(CH_2)_2OC(O)CH_2$), 60.3 ($CH_2(CH_2)_2OAr$), 61.8 ($CH_2OC(O)CH_2$), 63.0 (C_e), 64.6 (CH_2OAr), 98.1 and 98.3 (two C_{sp2}C(O) in macrocycle), 112.9 (C_b), 124.0 (C_h), 130.7 (C_g), 132.2 (C_c), 139.6 (C_d), 144.1 (C_f), 148.3 (C_i), 154.9 br (CH = N), 156.6 (C_a), 167.6 and 167.7 (two $C_{sp2}C$ = O at macrocycle), 171.6 ($C(O)CH_2$). The NMR signals assignment was supported by ^{1}H–^{13}C HSQC correlation spectra ($CDCl_3$, 600/150 MHz).

9Cu$_2$: This compound was synthesized from **6Cu** following the procedure described for **9Ni$_2$**. Yield 49%. Anal. Calc. for $C_{116}H_{142}Cu_2N_8O_{14}S_2\ 2H_2O$ (2099.7): C, 66.36; H, 7.01; N, 5.34. Found: C, 66.40; H, 7.00; N, 5.08%. TOF MS FD$^+$ (CH_2Cl_2, *m*/*z*): 2060.5 [$C_{116}H_{142}Cu_2N_8O_{14}S_2$]$^+$.

10Ni: Complex **3Ni** (396 mg, 0.746 mmol) was dissolved in 20 ml CH_2Cl_2. A solution of sodium azide (1.212 g, 25 eq) and tetrabutylammonium bromide (0.241 g, 1 eq) in 6 ml H2O was added. This two phase system was degassed and stirred vigorously under argon atmosphere for 4 days. The organic phase was then washed with 50 ml H2O, dried over MgSO4, and concentrated. The residue was dissolved in methanol (10 ml) and the mixture left for crystallization upon evaporation of solvents. Crystals of the product were filtered, washed with Et2O and dried in vacuo. Yield: 334.6 mg (94%). *Anal.* Calc. for $C_{18}H_{25}N_7NiO_5$ (478.1): C, 45.22; H, 5.27; N, 20.51. Found: C, 45.29; H, 5.26; N, 20.35%. TOF MS FD$^+$ (CH_2Cl_2, *m*/*z*): 477.1 [$C_{18}H_{25}N_7NiO_5$]$^+$. ^{1}H NMR ($CDCl_3$, 500 MHz, δ (ppm)): 1.88 t (2H, *J* = 6.0 Hz, CH_2CH_2OH), 1.96 t (2H, *J* = 6.5 Hz, $CH_2CH_2N_3$), 2.52 t (1H, *J* = 6.2 Hz, OH), 3.39 s (8H, NCH_2CH_2N), 3.41 t (2H, *J* = 6.5 Hz, CH_2N_3), 3.66 q (2H, *J* = 5.9 Hz, CH_2OH), 4.25 t (2H, *J* = 6.2 Hz, $CH_2(CH_2)_2N_3$), 4.34 t (2H, *J* = 6.0 Hz, $CH_2(CH_2)_2OH$), 7.81 s and 7.82 s (2 × 2H, CH = N). ^{13}C NMR ($CDCl_3$, 125 MHz, δ (ppm)): 28.6 ($CH_2CH_2N_3$); 32.5 (CH_2CH_2OH); 48.5 (CH_2N_3); 58.7, 58.8, 58.9, 59.8 and 60.3 (two $C(O)OCH_2$, two NCH_2, CH_2OH); 98.0 and 98.1 (two C_{sp2}C(O) in macrocycle); 154.9 and 155.0 (two CH=N); 167.5 and 168.5 (two C=O).

10Cu complex was also obtained following the procedure for **10Ni**. Yield 87%. *Anal.* Calc. for C, 44.76; H, 5.22; N, 20.30. Found:

C, 44.62; H, 5.12; N, 20.12%. TOF MS FD$^+$ (CH_2Cl_2, *m*/*z*): 482.1 $[C_{18}H_{25}CuN_7O_5]^+$.

12Ni$_3$: 237.1 mg of **10Ni** (0.496 mmol), 118.6 mg of **11Ni** (0.5 eq), and 305.3 mg (benzyltriazolyl)methylamine (1 eq) were dissolved in the mixture of 9.5 ml CH_2Cl_2 and 4.75 ml MeOH. 349.1 mg of copper(I) iodide (3.2 eq) was added, and the mixture was stirred under argon in room temperature. After 2 days, additional portion of CuI (109 mg, 1 eq) was added, and the reaction was carried out for yet another 2 days. Than 20 ml CH_2Cl_2 and 10 ml MeOH were added to the suspension, solids were filtrated, and the filtrate was evaporated to dryness. The remaining brown solid was dissolved in small amount of CH_2Cl_2 containing 2% of MeOH, followed by purification on silica gel DCVC column. Gradient elution from 2% to 10% of MeOH in CH_2Cl_2 was used, and the product **12Ni$_3$** was collected as the fourth colored fraction. After partial evaporation of the solvent the product was precipitated with hexane, filtered, and dried in vacuo. Yield: 41.1 mg (12%). *Anal.* Calc. for $C_{56}H_{72}N_{18}Ni_3O_{14}$ (1397.4): C, 48.13; H, 5.19; N, 18.04. Found: C, 48.20; H, 5.22; N, 17.98%. TOF MS FD$^+$ (CH_2Cl_2, *m*/*z*): 1394.3 $[C_{56}H_{72}N_{18}Ni_3O_{14}]^+$, 1417.3 $[C_{56}H_{72}N_{18}Ni_3O_{14}{\cdot}Na]^+$, 697.2 $[C_{56}H_{72}N_{18}Ni_3O_{14}]^{2+}$, 720.2 $[C_{56}H_{72}N_{18}Ni_3O_{14}{\cdot}2Na]^{2+}$. ^{1}H NMR ($CDCl_3$, 600 MHz, δ (ppm)): 1.86 p (4H, *J* = 6.0 Hz, CH_2CH$_2$OH), 2.26 p (4H, *J* = 6.3 Hz, CH$_2$CH_2CH$_2$N), 3.11 t br (4H, CH_2C$_{sp2}$), 3.35 s (16H, N(CH$_2$)$_2$N in terminal complex units), 3.38 (8H, N(CH$_2$)$_2$N in central complex unit), 3.65 t (4H, *J* = 5.7 Hz, CH_2OH), 4.19 t (4H, *J* = 5.7 Hz, CH_2(CH$_2$)$_2$N), 4.32 t (4H, *J* = 6.0 Hz, CH_2(CH$_2$)$_2$OH), 4.40 t (4H, *J* = 6.6 Hz, CH_2CH$_2$C$_{sp2}$), 4.42 t (4H, *J* = 7.8 Hz, (CH$_2$)$_2$CH_2N), 7.41 s br (2H, triazole proton), 7.72 s (4H, CH = N in central complex unit), 7.75 s and 7.79 s (8H, CH = N in terminal complex units). ^{13}C NMR ($CDCl_3$, 150 MHz, δ (ppm)): 25.9 (*C*H$_2$C$_{sp2}$), 29.9 (CH$_2$*C*H$_2$CH$_2$N), 32.4 (*C*H$_2$CH$_2$OH), 47.7 ((CH$_2$)$_2$*C*H$_2$N), 58.75, 58.77 and 58.83 (N(*C*H$_2$)N and (CH$_2$)$_2$*C*H$_2$OH), 59.87 and 59.92 (*C*H$_2$(CH$_2$)$_2$OH and *C*H$_2$(CH$_2$)$_2$N), 62.0 (*C*H$_2$CH$_2$C$_{sp2}$), 97.8, 98.0, and 98.1 (three different *C*$_{sp2}$C(O) in macrocycles), 121.8 (triazole *C*H), 145.5 (CH$_2$-*C*$_{sp2}$), 154.9 and 155.0 (CH=N in macrocycles), 167.5, 167.6, and 168.5 (three C=O).

3. Results and discussion

3.1. Synthetic route towards non-symmetrical complexes of Cu(II) and Ni(II)

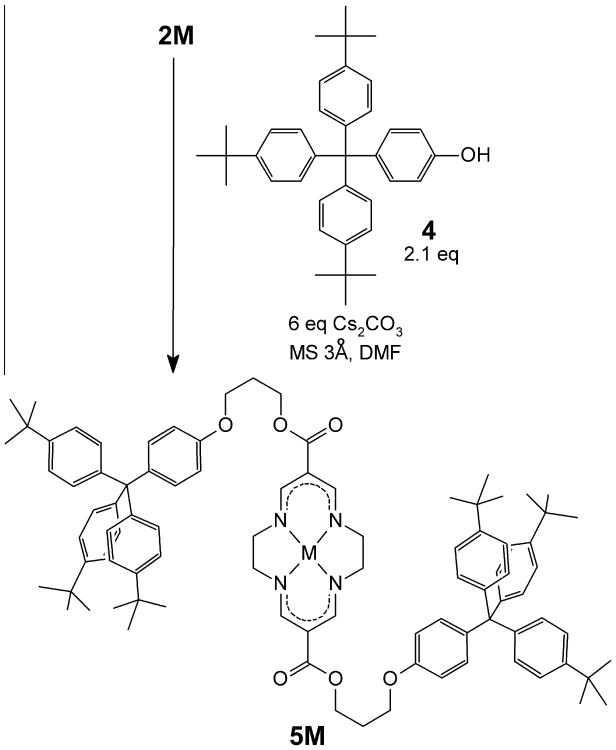
The synthetic route towards non-symmetrically functionalized tetraazamacrocyclic complexes was found by studying mesylation of diols **1M** (Scheme 2). Typical mesylation of **1M** in dichloromethane, carried out with 0.8–1.0 equivalent of mesyl chloride, leads preferentially to undesired symmetrical derivatives – dimesylates **2M**, suggesting that monomesylate intermediate (**3M**) is more reactive towards mesyl chloride, than the substrate **1M**. Yields of monomesylates **3M** were unsatisfactory – between 20% and 25%, what is even two times lower than what one might expect from purely statistical distribution. The ratio of products was nearly independent from the rate of mesyl chloride addition, and did not improved even when the reactant was slowly added with the help of syringe pump. Our experiments show that the well-known Ag_2O-aided method for monotosylation of symmetrical diols [17], did not improved the yields either. Dimesylated or ditosylated products were formed preferentially, showing that Ag_2O had no influence on the chemical behavior of diols **1M**. However, when the mesylation of **1M** is carried out with 0.8 eq of mesyl chloride in neat, anhydrous pyridine at 0 °C, desired monomesylates **3Cu** and **3Ni** are formed with decent yields (Scheme 2) – conversion of MsCl to **3M** is about 70%. That result is better than 1:2:1 distribution of diol to monomesylate to dimesylate, expected if only statistical factors would play role during reaction course.

3.2. Synthesis of linear complexes

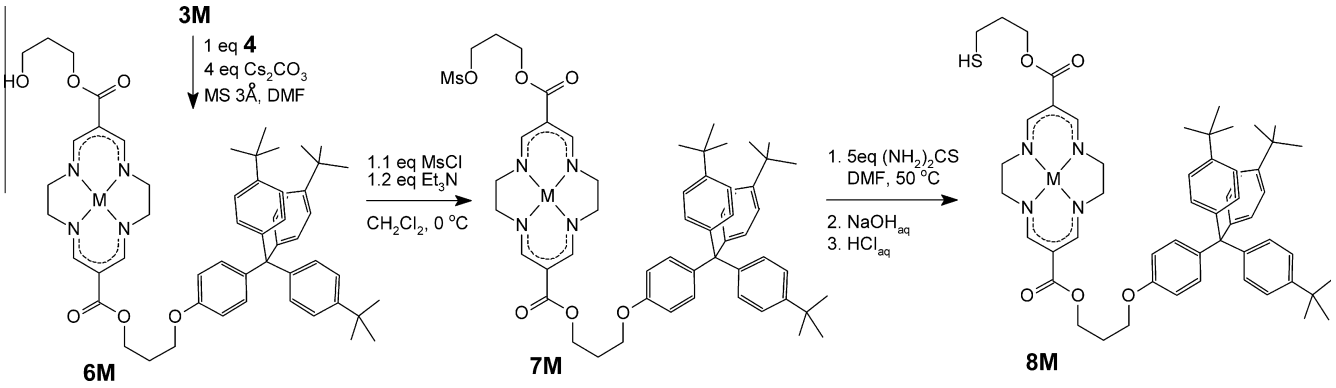
Intercalation of π-acceptors into the monolayer of simple dithiol counterparts of **1Ni** and **1Cu** is relatively limited due to the well-packed structure of the SAM film. Here, we present our recent advances in chemical synthesis of new derivatives of neutral tetraazamacrocyclic complexes of copper(II) and nickel(II), aimed at designing molecules potentially capable of formation of SAMs with inherent free spaces built between units of π-donor complexes. That would facilitate intercalation of π-electron deficient molecules into the SAM film. We have also investigated the synthesis of compounds containing two or three units of electron rich tetraazamacrocyclic complex linearly arranged within one molecule, for future studies in their ability to participate in intermolecular interactions, when influenced by the increased number of π-donor units.

For introduction of bulky end groups to complex molecules we have chosen tris(p-*tert*-butylphenyl)(4-hydroxyphenyl)methane (**4**). This compound was obtained following a known two-step synthesis [16]. Reactions of **4** with dimesylates **2M** were carried out in presence of a cesium carbonate in anhydrous DMF (Scheme 3). Neutral complex derivatives containing two bulky end groups were obtained with 69% yield for **5Cu** and 71% for **5Ni**. The reactions were carried out for 3 days at room temperature, since elevated temperatures led to decrease of the yield, due to partial degradation of dimesylates. The analogous reaction of **2Ni** with commercially available tritylphenol was also tested, and it proceeded with a similar yield. However, the product substituted with large number of aromatic rings, and containing no aliphatic substituents was sparingly soluble in all common solvents.

The monomesylates **3M** have been also used to synthesize monothiols **8M**. Complex **3M** was at first reacted with tris(*p*-*tert*-butylphenyl)(4-hydroxyphenyl)methane, then the remaining hydroxyl group mesylation was followed by substitution towards isothiouronium salt, alkaline hydrolysis of the salt, and protonation of the resulting thiolate (Scheme 4).



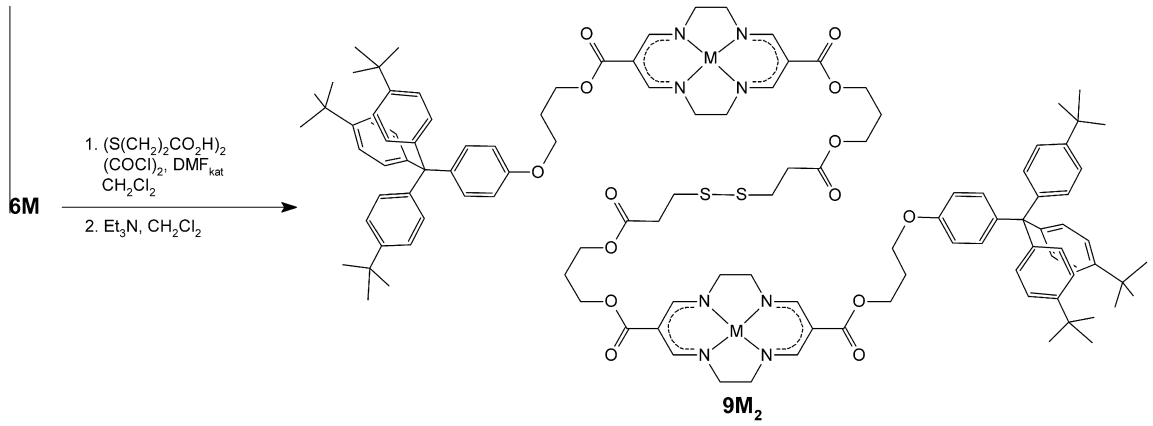
Scheme 3.



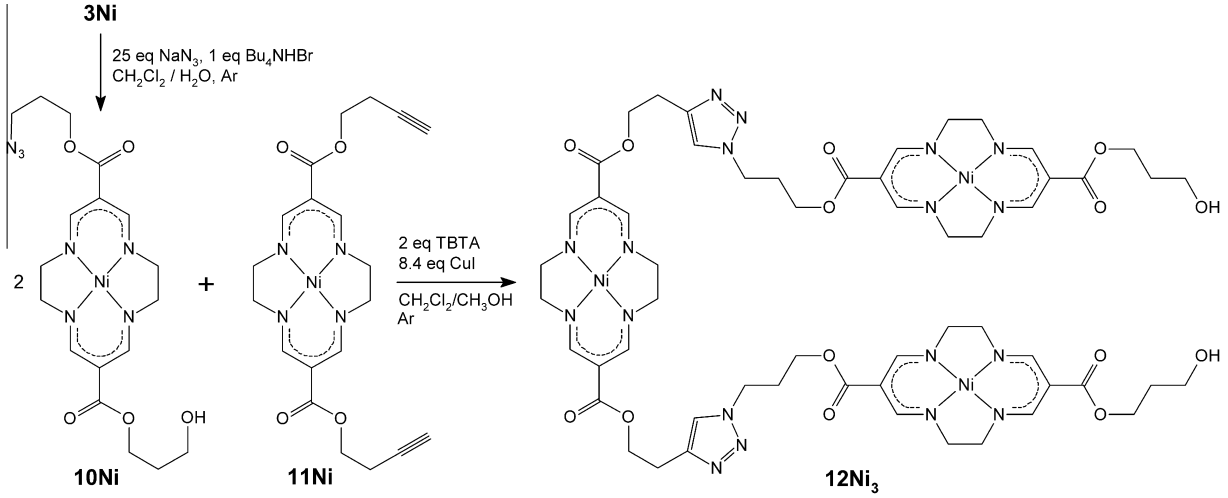
Scheme 4.

Additionally, alcohols **6M**, intermediate products in this series of reactions, were used as substrates in the synthesis of dinuclear complexes **9Cu$_2$** and **9Ni$_2$** (Scheme 5). These compounds were synthesized by coupling two molecules of **6M** with freshly generated 3,3′-dithiodipropionic acid dichloride, providing homodinuclear complexes with a linker containing a disulfide bond. Both **9Cu$_2$** and **9Ni$_2$** were synthesized with decent yields (49% and 56%, respectively). Unfortunately, synthesis of heterodinuclear complex **9CuNi** couldn't be realized by similar reaction of acid dichloride with an equimolar mixture of **6Ni** and **6Cu**, since separation of compounds from statistical mixture of **9Ni$_2$**, **9Cu$_2$** and **9CuNi** was not successful. Disulfides are useful in self-assembly of monolayers, since they anchor to the gold surface. It is worthwhile mentioning that linear molecules **9M$_2$**, as well as compounds **5M** can be used in future for exploiting their π-donor properties in solutions and solid state, as well as they may function as potential rotaxane axels interacting with macrocycles containing electron deficient moieties.

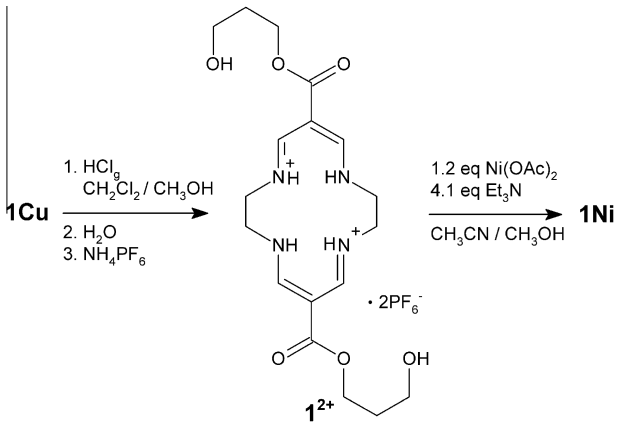
In order to further develop linear arrangement of macrocylic metal complex units we have used 1,3-dipolar Huisgen cycloaddition. The monomesylate **3Ni** was transformed by standard procedure into monoazide **10Ni**, which has been then used in cycloaddition reaction with diacetylene derivative **11Ni** (Scheme 6). This reaction was cactalyzed by tris(benzyltriazolyl)methylamine (TBTA), which prevents oxidation and disproportionation of copper(I) [18]. Linear



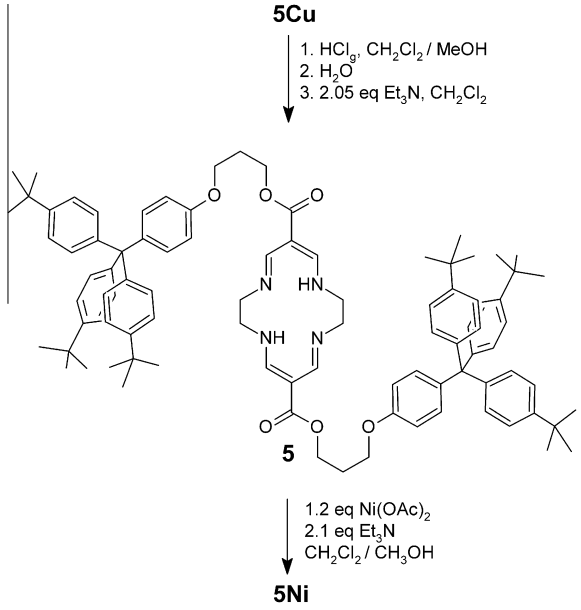
Scheme 5.



Scheme 6.



Scheme 7.



Scheme 8.

product **12Ni$_3$**, containing three neutral complex units was isolated with 12% yield.

3.3. Demetallation of copper complexes

In highly acidic conditions copper(II) complexes are prone to demetallation, which does not occur in case of nickel(II) complexes under the same conditions. The demetallation reaction is carried out by bubbling HCl gas through the solution of a copper complex in the mixture of dichloromethane with methanol. After few minutes of bubbling characteristic pink color changes into yellow, coming from the tetrachlorocopper(II) dianion. Protonated dicationic ligand is produced simultaneously. In case of **1Cu** complex with polar terminal groups, this chloride was soluble in water, thus **1^{2+}** ligand was precipitated as hexafluorophosphate salt upon addition of NH4PF6 (Scheme 7).

In case, when the terminal groups of the complex are non-polar, like bulky groups in **5Cu**, the yellow precipitate of $CuCl_4^{2-}$ salt is formed during HCl gas bubbling. This precipitate quickly transforms into dichloride when stirred in water. However, since dichloride of **5^{2+}** ligand was poorly soluble in any common solvent it was separated as neutral ligand **5** upon neutralization with two equivalents of triethylamine and filtration through short silica gel column (Scheme 8).

Since demetallation reaction is reversible, it is possible to regenerate copper(II) or nickel(II) complex from the ligand obtained. Indeed, we have succeeded in the synthesis of **1Ni** complex starting from **1Cu**, and going through **1^{2+}(PF$_6^-$)$_2$** salt with 78% overall yield, as well as in demetallation of **5Cu** complex to neutral ligand **5**, followed by recomplexation with Ni^{2+} ions to form **5Ni** complex with 59% overall yield. Therefore the demetallation reaction of copper(II) tetraazamacrocyclic complexes and its universal character provide a shortcut that allows obtaining nickel(II) complexes from their copper(II) counterparts, instead of repetition of the whole reaction sequences for nickel(II) starting materials.

The structures of synthesized complexes and free ligands were established in terms of elemental analyses, reactions and spectral evidence. The diamagnetic nickel(II) complexes and demetallated ligands were characterized by ^{1}H and ^{13}C NMR spectra, and the signals assignment was supported by 2D ^{1}H–^{13}C correlation spectra. All studied compound were also identified by electrospray (ESI) or field desorption (FD) mass spectra, especially useful in the case of copper(II) complexes. Since, due to paramagnetic properties of

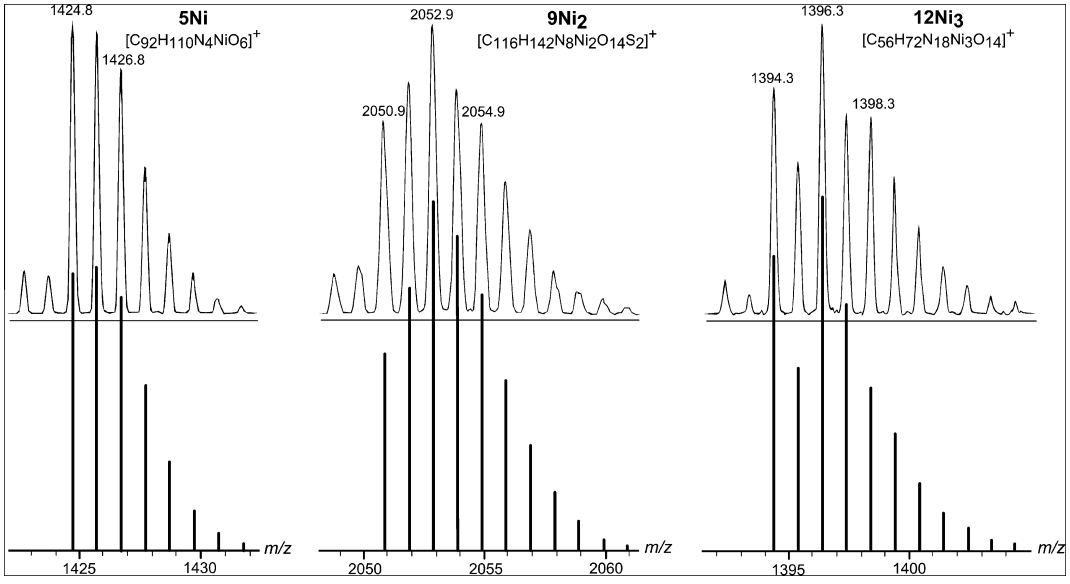


Fig. 1. Experimental (above) and calculated (below) isotopic profiles of [M]$^+$ peaks in FD mass spectra of mono-, di- and tri-nuclear nickel complexes **5Ni**, **9Ni$_2$**, **12Ni$_3$**.

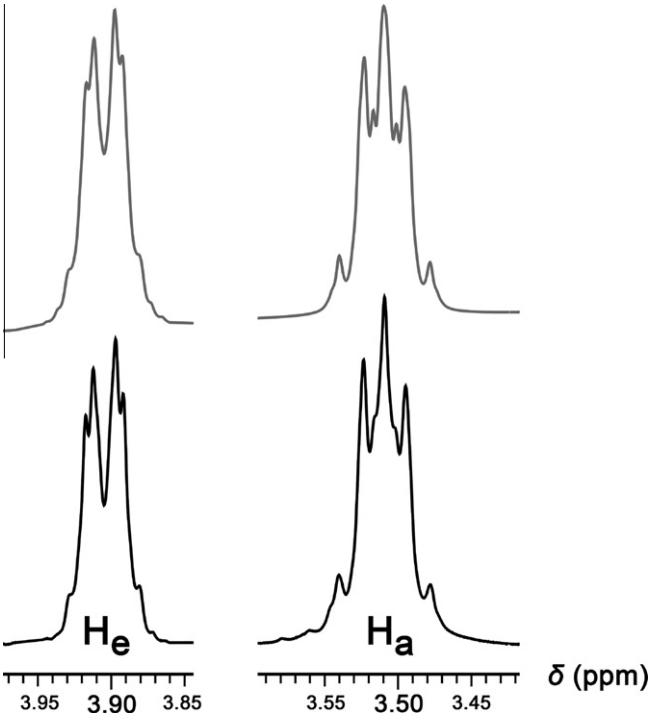


Fig. 2. Simulated (above) and experimental (below) shapes of signals of axial (H_a) and equatorial (H_e) protons in ethylenediamine bridge in 1H NMR spectra of diol $\mathbf{1}^{2+}$ (CD_3CN, 600 MHz, 25 °C).

these complexes the NMR data were not available. In all instances, *m*/*z* values as well as the isotopic profiles of mass peaks were consistent with calculated ones, as is shown for mono-, di- and tri-nuclear nickel(II) complexes **5Ni**, **9Ni$_2$**, **12Ni$_3$** in Fig. 1.

As expected, in neutral ligand **5** tautomeric exchange of NH protons between nitrogen atoms was a fast process compared to the NMR time scale, resulting in averaged signals both for ^{1}H, and ^{13}C nuclei in imine/enamine groups and ethylenediamine bridges at 25 °C. On the other hand, in protonated molecule $\mathbf{1}^{2+}$ dynamical exchange of protons between nitrogen atoms does not occur. Therefore the signal of imine protons CH=N is observed as a doublet with a coupling constant to NH protons, $^3J_{H,H}$ = 15.41 Hz. Moreover, in contrast to what was observed in ^{1}H NMR spectra of nickel(II) complexes and neutral ligand **5**, signals of protons of ethylenediamine bridges appear as two separate multiplets at 3.51 and 3.91 ppm. The values of coupling constants have been determined, and the shape of these multiplets simulated by iterative fitting to experimental spectrum using a homemade software (Fig. 2).

Protons in NCH_2CH_2N bridge are coupled geminally with a calculated constant $^2J_{H,H}$ = −14.43 Hz. Vicinal coupling constants are $^3J_{H,H}$ = 2.04, 2.35 Hz for protons in gauche, and 10.97 Hz for protons in anti positions. Protons of methylene groups are also coupled to NH protons with $^3J_{H,H}$ = 3.94 and 8.44 Hz. All coupling constants and chemical shifts are summarized in Fig. 3B.

Obtained $^3J_{H,H}$ values were used to determine the geometry of ethylenediamine bridges, using 'Generalized $^3J_{H,H}$ calculation according to Haasnoot et al.' script [19,20]. Calculated values of dihedral angles in NCH_2CH_2N bridge are equal to 57°, 71° and 162° (Fig. 3A). The protonated macrocyclic ring in $\mathbf{1}^{2+}$ cation conformation consistent with these values is shown in Fig. 3B. Similar conformation was previously established for the methyl ester analog of $\mathbf{1}^{2+}$ by X-ray crystallography [10]. The unsaturated, planar parts of the macrocycle adopt *s-trans* conformations with all NH protons pointing on the outside of a ring, whereas in the free ligand the remaining two protons form strong hydrogen bonds between nitrogen atoms and are located inside of the macrocyclic ring [10].

4. Conclusions

The synthetic route towards non-symmetrically functionalized tetraazamacrocyclic complexes was found by mesylation of symmetric diols **1M** in neat, anhydrous pyridine at 0 °C. Selective monomesylation allowed unsymmetrical elaboration of macrocylic ligand superstructure. This synthetic strategy was used to obtain macrocyclic copper(II) and nickel(II) complexes substituted with bulky terminal group on one side 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 selectively monomesylated intermediates. It is our intention to use such linear molecules as rotaxane axels interacting with macrocycles containing electron deficient moieties.

The demetallation reaction of neutral copper(II) tetraazamacrocyclic complexes provide a shortcut that allows obtaining complexes with another transition metal ions from their copper(II) counterparts.

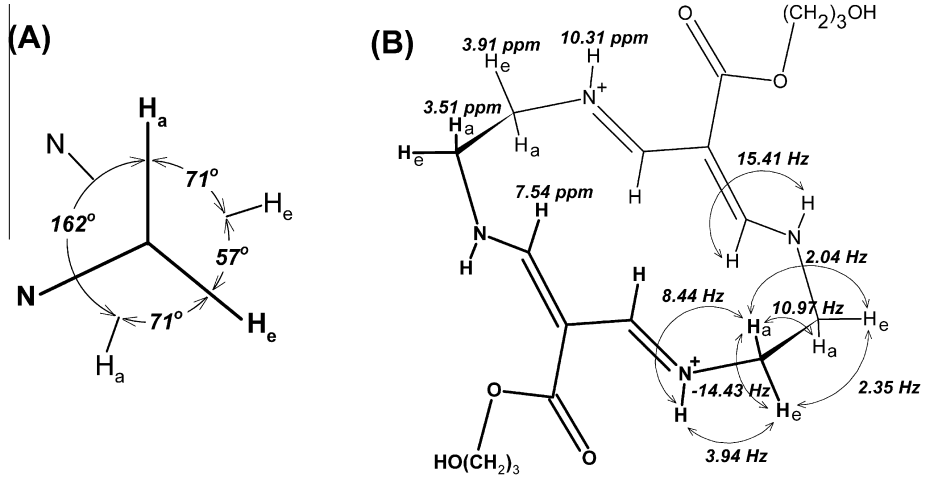


Fig. 3. Torsion angles in ethylenediamine bridge as seen with Newman projection (A), and schematic structure of $\mathbf{1}^{2+}$ cation, with chemical shifts of protons in macrocycle, and all coupling constants between them (B).

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