New biionic transition metal complexes based on the salen ligands: synthesis and application as synthons in the preparation of chiral homo- and heterobimetallic systems

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A new approach was used for the development of chiral homo- and heterobimetallic systems resulting in the preparation of four original bimetallic systems, two of which were studied by X-ray diffraction.

Key words: chiral reactants, bimetallic complexes, binuclear catalytic systems, salen complexes, biionic systems.

Studies in the field of asymmetric metal complex catalysis have been conducted already for quite a while, and various efficient chiral catalytic systems have been developed since then. $^{1-4}$ It was found that the best results (the yields >99%, the ee up to 99%) are shown by binuclear catalytic systems, in which the metal ions are fixed in space with respect to each other, 5-7 and such a fixation of metals can be due to either the covalent bond system, $^{8-12}$ or noncovalent¹³ interactions. In the overwhelming majority of cases, such binuclear catalytic systems are homobimetallic. In the first place, this is because the polydentate ligands capable of retaining two (or more) metal ions at the fixed distance by the covalent bond system are used for their synthesis, but such an approach does not guarantee obtaining heterobimetallic systems. As of this moment, only a limited number of methods for the synthesis of heterobimetallic systems are known;^{14–18} however, most of them cannot be virtually used for the synthesis of systems based on two different transition metals.

Taking this into account, we set us a purpose to develop a simple method for the synthesis of bimetallic systems, which would have allowed us to equally easily obtain both the homo- and heterobimetallic systems.

Our approach is based on the idea of mutual fixation of two separate molecules of metal complexes with respect to each other by electrostatic interaction. Initially, complexes of different metals are prepared separately, and only then they are used to form bimetallic homo- or heterobimetallic systems. The authors of the work¹⁹ used an approach, which has something in common with ours, but differing in the fact that a chiral organic anion of the BINOL phosphoric acid derivative was a counter ion at the achiral manganese complex in the "ion-pair" catalyst A developed by the authors.⁹



We have chosen complexes of chiral tetradentate ligands, which are the Schiff bases of (R,R)-diaminocyclohexane with substituted salicylaldehydes (salens) bearing charged functional groups (**B**), as the first model systems.



Published in Russian in Izvestiya Akademii Nauk. Seriya Khimicheskaya, No. 8, pp. 1587–1593, August, 2011. 1066-5285/11/6008-1612 © 2011 Springer Science+Business Media, Inc. Sulfo groups were chosen as the anionic and trimethylammonium groups as the cationic groups. The choice of such a system was stipulated by the fact that salen-based catalysts in most cases display excellent results in the enantioselective formation of C–C and C–N bonds (see Refs 20 and 21).

Results and Discussion

Synthesis of ligands with anionic groups involves the use of 3-*tert*-butyl-5-sulfosalicylaldehyde disodium salt as



the starting compound. Such a Schiff base (1) has been described earlier,²² but we modified this method using (1R,2R)-1,2-diaminocyclohexane as a free base, as it is shown in Scheme 1, rather than its salt with (R,R)-tartaric acid, as in the original²² work.

This method seems to be more simple and convenient, since it does not require additional purification of ligand **1** from the tartrate impurities.

Further, we developed a procedure for the synthesis of the second ligand **5** required for the study (Scheme 2).

It was found that direct reduction of 3-tert-butyl-5-nitrosalicylaldehyde with hydrogen with simultaneous reductive methylation of the amino group with formaldehyde leads to the key intermediate product, viz., 3-tert-butyl-5dimethylaminosalicylaldehyde; however, it has proved unstable, and we rejected this approach. That is why we have chosen the method using a salicylaldehyde triacetyl derivative, viz., 2-(diacetoxymethyl)-6-tert-butyl-4-nitrophenyl acetate (2),²³ as the starting compound. Compound 2 was also reduced with hydrogen with simultaneous methvlation, that allowed us to obtain 2-(diacetoxymethyl)-6tert-butyl-4-(dimethylamino)phenyl acetate (3) stable even during prolonged storage. The reaction of compound 3 with (1R,2R)-1,2-diaminocyclohexane (R,R)-tartrate in aqueous ethanol in the presence of potash led to (1R,2R)-1,2-bis-{[3-tert-butyl-5-(dimethylamino)-2hydroxyphenyl]methyleneamino}cyclohexane (4). The reaction of methyl iodide with compound 4 in MeCN afforded the target compound 5. Note that, despite seem-

Scheme 2



Reaction conditions: *i*. (MeCO)₂O, H₂SO₄; *ii*. HCHO, H₂, Pd/H, EtOH; *iii*. (1*R*,2*R*)-1,2-diaminocyclohexane (*R*,*R*)-tartrate, K₂CO₃, EtOH, H₂O; *iv*. MeI, MeCN.

ing feasibility and simplicity of the synthesis, compounds 2-5 were obtained for the first time.

Thus obtained ligands 1 and 5 were converted to the corresponding complexes upon the action of copper(II) and nickel(II) acetates in methanol (Scheme 3).

Scheme 3



1: $R' = Na$, $R = SO_3Na$ 5: $R' = H$, $R = N^+Me_3I^-$	Com- pound	R	М
	6a	SO ₃ Na	Ni
	6b	SO ₃ Na	Cu
	7a	N ⁺ Me ₃ I ⁻	Ni
	7b	N ⁺ Me ₃ I ⁻	Cu

Complexes 6 and 7 are colored powders, poorly soluble in both water and most organic solvents, except methanol. These complexes were obtained for the first time and characterized by elemental analysis, UV spectroscopy, and NMR (for compounds 6a and 7a).

For the synthesis of binuclear metal-containing systems, solutions of complexes 6 and 7 in methanol were mixed in pairs in equimolar ratios, which led to the formation of compounds 8-11 as precipitates (Scheme 4).

Elemental analysis of complexes 8-11 showed that these compounds contain no iodine and in complexes 9 and 10 the ratio of metals Cu : Ni = 1 : 1. Since such compounds were obtained for the first time, it was of interest to study their structures. Single crystals of complexes 9 and 10 were grown from methanol solutions. The structures of the synthesized compounds are given in Figs 1 and 2.

The X-ray diffraction study showed that the planes of the complex "halves" are at a distance of about 3.6 Å with respect to each other, whereas the distance between the metal atoms is 5 Å. In both complexes (9 and 10), one methanol molecule is coordinated to the Cu atom.

In conclusion, we developed a new method for the design of bimetallic salen systems, which allows the synthesis of both homo- and heterobinuclear catalytic systems with equal simplicity. At the present time, we conduct studies on catalytic activity and stereodifferentiating ability of the obtained chiral binuclear metal complex systems in the reactions with the C—C bond formation.

Experimental

The ¹H and ¹³C NMR spectra were recorded on a Bruker AVANCE 300 spectrometer (300 MHz and 75.5 MHz, respectively) using residual signals for the undeuterated solvent as an internal standard (¹H NMR). Optical rotation was measured on a Perkin—Elmer 241 polarimeter in a 5-cm thermostated cell at 25 °C. Elemental analysis for the compounds obtained was performed in the Elemental Analysis Laboratory of the A. N. Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences. The C, H, and N contents were determined on a Carlo Erba 1106 instrument, the S content was de-



Scheme 4

MeOH

-2 NaI



Nu., Nu.,

NMe₃I

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Fig. 1. The structure of complex 9. Hydrogen atoms and the solvent molecules are not shown.



Fig. 2. The structure of complex 10. Hydrogen atoms and the solvent molecules are not shown.

termined by the Schöniger method, the Cu and Ni contents, by X-ray fluorescence analysis on a VRA 30 instrument. Electronic absorption spectra were recorded on a Specord M-40 spectrometer (Carl Zeiss, Jena). All the starting reactants (Aldrich or Acros) were used without additional purification. (R,R)-Diaminocyclohexane was obtained by resolution of racemic 1,2-di-

aminocyclohexane through the formation of diastereomeric salt with (1R,2R)-tartaric acid²⁴ and subsequent liberation of the free base, *i.e.*, (R,R)-diaminocyclohexane, using the known procedure.²⁵ According to the GLC data, the enantiomeric purity of (1R,2R)-cyclohexanediamine in the formed salt is 99% (a 25 m×0.23 mm ID quartz capillary column, 12 µm DP-TFA- β-CD, $T_{col} = 140$ °C, N₂ carrier gas, 1.8 atm, retention time 11.2 min). 3-*tert*-Butyl-5-sulfosalicylaldehyde disodium salt was obtained using the known procedure.²² 3-*tert*-Butyl-5-nitro-salicylaldehyde was obtained according to the standard procedure by nitration of 3-*tert*-butylsalicylaldehyde in acetic acid.²⁶ Properties of the starting compounds obtained by these procedures completely corresponded to the literature data.

The unit cell parameters and intensities of reflections for the crystals of compounds 9 and 10 were measured on a Bruker SMART APEX II CCD automatic diffractometer (T = 100 K, $\lambda Mo\text{-}K\alpha$ radiation, graphite monochromator, $\phi\text{-}$ and $\omega\text{-}scan$ technique). The absorption correction was applied using the SADABS program.²⁷ The basic crystallographic data are given in Table 1. The structures of the compounds were solved by direct methods and refined by the full-matrix least squares method with anisotropic displacement parameters for nonhydrogen atoms. Crystals of both compounds contain two independent formula units per asymmetric unit. Two of four sulfo groups in different anions of compound 9 and all four sulfo groups in the anions of compound 10 are disordered over two positions related by the rotation around the C—S single bond with occupancies of 0.5: 0.5, 0.5: 0.5, 0.7: 0.3, 0.5: 0.5, 0.7: 0.3, 0.5: 0.5, 0.5: 0.5, 0.7: 0.3, 0.5: 0.5; 0.5: 0.5; 0.5;0.5: 0.5, 0.7: 0.3, and 0.5: 0.5, respectively. Crystals of both compounds contain methanol and water solvent molecules. In the crystal of compound 10, twelve methanol solvent molecules (one of which has partial occupancy of 0.5) and ten water solvent molecules (one of which is disordered over two positions

with occupancies of 0.6:0.4 and one has partial occupancy of 0.5) were refined with anisotropic displacement parameters for nonhydrogen atoms. Methanol and water solvent molecules in the crystal of compound 9 are considerably disordered and it was impossible to correctly refine their positions in the framework of the experiment performed. Therefore, the contribution of these molecules to the total scattering from the crystal of compound 9 was removed using the SQUEEZE program implemented in the PLATON98 program package.²⁸ The total amount of solvent molecules in the crystal of compound 9 was determined based on the data from the SQUEEZE program, which showed that the number of electrons in the free volume of its unit cell is equal to 158, as well as based on the isostructurality of crystals of compounds 9 and 10 (see Table 1). The hydrogen atoms in methanol and water solvent molecules in compound 10 were located in the difference Fourier maps and refined with fixed positional and thermal parameters. The other hydrogen atoms in both compounds were positioned geometrically and refined isotropically with the fixed positional (the riding model) and thermal $(U_{iso}(H) =$ = $1.5U_{eq}(C)$ for the CH₃ groups and $U_{iso}(H) = 1.2U_{eq}(C)$ for all other groups) parameters. The absolute structures of compounds $9 \cdot 6CH_3OH \cdot 5H_2O$ and $10 \cdot 5.75CH_3OH \cdot 4.75H_2O$ were determined by the refinement of the Flack parameter (see Table 1). All the calculations were performed using the SHELXTL program package.²⁹ The tables of the atomic coordinates, bond distances, bond and torsion angles, and anisotropic temperature parameters

Table 1. Basic crystallographic data and structure refinement statistics for compounds 9.6CH₃OH \cdot 5H₂O and 10.5.75CH₃OH \cdot 4.75H₂O

Compound	9 •6CH ₃ OH•5H ₂ O	10 • 5.75CH ₃ OH • 4.75H ₂ O
Molecular formula	C ₆₉ H ₁₂₄ N ₆ O ₂₂ S ₂ NiCu	C _{68 75} H _{122 5} N ₆ O _{21 5} S ₂ NiCu
Crystal size, mm	0.02×0.25×0.25	0.15×0.18×0.21
Molecular weight	1576.11	1563.60
T/K	100	100
Crystal system	Triclinic	Triclinic
Space group	$P\overline{1}$	$P\overline{1}$
a/Å	8.947(6)	8.6649(6)
b/Å	15.316(11)	15.4052(10)
c/Å	29.58(2)	30.615(2)
α/deg	77.166(16)	78.719(2)
β/deg	84.593(16)	87.894(2)
γ/deg	88.734(16)	88.695(2)
$V/Å^3$	3935(5)	4004.5(5)
Ζ	2	2
$d_{\rm calc}/{\rm g}~{\rm cm}^{-3}$	1.330	1.297
F(000)	1690	1676
μ/mm^{-1}	0.636	0.624
$2\theta_{\text{max}}/\text{deg}$	50	53
Number of reflections		
measured	33911	40021
independent	27200	32249
with $I > 2\sigma(I)$	13820	19512
Number of refinement parameters	1285	1720
$R_1 (I \ge 2\sigma(I))$	0.0771	0.0718
wR_2 (all reflections)	0.2033	0.1846
GOOF	0.851	1.003
Flack parameter	0.036(15)	0.028(14)
T_{\min}/T_{\max}	0.857/0.987	0.880/0.912

for compounds 9.6 CH₃OH.5H₂O and 10.5.75CH₃OH.4.75H₂O were deposited with the Cambridge Structural Database.

(1R,2R)-Cyclohexane-1,2-diylbis(2-azaethenyl-3-tert-butyl-2-hydroxybenzo-5-sulfonic acid) disodium salt (1). (1R,2R)-1,2-Diaminocyclohexane (151 mg, 1.32 mmol) was added to a solution of 3-tert-butyl-5-sulfosalicylaldehyde disodium salt (800 mg, 2.65 mmol) in methanol (5 mL). The mixture was refluxed for 6 h, then the solvent was evaporated on a rotary evaporator, and the residue that was obtained was dried using a vacuum oil pump to yield a dark yellow product (870 mg, 96%), which was used without additional purification, $[\alpha]_D^{25}$ –152 (c 0.01 MeOH). ¹H NMR (300 MHz, CD₃OD), δ: 8.45 (s, 2 H, C<u>H</u>N); 7.76 (d, 2 H, Ar, J=2.15 Hz); 7.61 (d, 2 H, Ar, J=2.14 Hz); 3.50–3.53 (m, 2 H, CH, diaminocyclohexane); 1.7-1.97 (m, 4 H, CH₂ diaminocyclohexane); 1.4-1.7 (m, 4 H, CH₂, diaminocyclohexane); 1.32 (s, 18 H, C(CH₃)₃). ¹³C NMR (75.5 MHz, CD₃OD), δ: 166.61, 163.64, 159.72, 156.85, 138.68, 135.63, 126.64, 118.82, 73.15, 35.94, 34.01, 29.71, 25.25. Found (%): C, 52.57; H, 5.61; N, 4.33; S, 9.91; Na, 7.32. C₂₈H₃₆N₂Na₂O₈S₂. Calculated (%): C, 52.65; H, 5.68; N, 4.39; S, 10.04; Na, 7.20.

2-(Diacetoxymethyl)-6-*tert***-butyl-4-**nitrophenyl acetate (2). 3-*tert*-Butyl-5-nitrosalicylaldehyde (2) (4.56 g, 20 mmol) was dissolved in acetic anhydride (6.6 mL) with heating to 50 °C. After **2** was completely dissolved, concentrated sulfuric acid (one drop) was added to the solution. The precipitate that formed was filtered off, washed with water, dried in air, and recrystallized from hexane to yield a cream product (5.28 g, 72%), m.p. 122–123 °C. ¹H NMR (300 MHz, CDCl₃), δ : 8.4 (s, 1 H Ar); 8.36 (s, 1 H, Ar); 7.76 (s, 1 H, C<u>H</u>(OCOCH₃)₂); 2.41 (s, 3 H, OCOC<u>H₃</u>); 2.12 (s, 6 H, (OCOC<u>H₃</u>)₂); 1.39 (s, 9 H, C(C<u>H₃</u>)₃). ¹³C NMR (75.5 MHz, CD₃Cl), δ : 169.17, 168.24, 151.66, 145.64, 144.76, 131.55, 124.28, 121.69, 83.75, 35.5, 30.21, 21.2, 20.64. Found (%): C, 55.64; H, 5.85; N, 3.73. C₁₇H₂₁NO₈. Calculated (%): C, 55.58; H, 5.76; N, 3.81.

2-(Diacetoxymethyl)-6-tert-butyl-4-(dimethylamino)phenyl acetate (3). A 10%Pd-C catalyst (0.6 g) was added to a solution of compound 2 (2.5 g, 6.8 mmol) and formaldehyde (5 mL) in ethanol (30 mL), and the reaction mixture was stirred for 72 h at room temperature and atmospheric pressure of hydrogen. The reaction progress was monitored by TLC using light petroleum-acetone (10:1) as an eluent. After the reaction was completed, the mixture was filtered from the catalyst, and the filtrate was concentrated to obtain a dark yellow oil, which was recrystallized from hexane to yield a cream product (2.1 g, 85%) with m.p. 93–94 °C. ¹H NMR (300 MHz, CDCl₃), δ: 7.71 (s, 1 H, CH(OCOCH₃)₂); 6.84 (s, 1 H, Ar); 6.8 (s, 1 H, Ar); 2.96 (s, 6 H, (OCOCH₃)₂); 2.33 (s, 3 H, 3 H, OCOCH₃); 2.09 (s, 6 H, $N(CH_3)_2$; 1.33 (s, 9 H, $C(CH_3)_3$). ¹³C NMR (75.5 MHz, CD₃OD), δ: 172.53, 170.22, 168.17, 150.18, 143.65, 139.22, 130.62, 114.57, 110.62, 86.91, 41.21, 36.08, 31.11, 21.53, 20.67. Found (%): C, 62.52; H, 7.53; N, 3.78. C₁₉H₂₇NO₆. Calculated (%): C, 62.45; H, 7.45; N, 3.83.

(1R,2R)-1,2-Bis-{[3-tert-butyl-5-(dimethylamino)-2-hydroxyphenyl]methyleneamino}cyclohexane (4). (R,R)-Diaminocyclohexane L-tartrate (361 mg, 2.74 mmol) and K₂CO₃ (3.78 g, 27.4 mmol) were dissolved in a water—ethanol mixture (1 : 1, 10 mL) with heating followed by the slow (dropwise) addition of a solution of compound 3 (1 g) in ethanol (10 mL) to the solution obtained. The reaction mixture was heated for 2 h at 80 °C, cooled, and kept for 16 h. The solution that was obtained was half concentrated, diluted with water to the initial volume, filtered, and washed with water and a small amount of ethanol to i d v e -1 a yellow product (527 mg, 37%). M.p. 110–112 °C, $[\alpha]_D^{25}$ –308 (c 0.01 MeOH). ¹H NMR (300 MHz, CDCl₃), δ: 8.25 (s, 2 H, CHN; 6.89 (d, 2 H, Ar, J = 2.9 Hz); 6.43 (d, 2 H, Ar, J = 2.9 Hz); 3.25-3.40 (m, 2 H, CH, diaminocyclohexane); 2.76 (s, 12 H, $N(CH_3)_2$; 1.82–2 (m, 4 H, CH₂, diaminocyclohexane); 1.5-1.8 (m, 4 H, CH2, diaminocyclohexane); 1.41 (s, 18 H, C(CH₃)₃). ¹³C NMR (75.5 MHz, CDCl₃), δ: 165.8, 153.3, 143.3, 137.5, 118.3, 114.6, 72.43, 42.4, 34.9, 33.1, 29.3, 24.3; Found (%): C, 73.62; H, 9.32; N, 10.66. C₁₉H₂₇NO₆. Calculated (%): C, 73.81; H, 9.29; N, 10.76.

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(1R,2R)-Cyclohexane-1,2-diylbis(2-azaethenyl)(3-tert-butyl-2-hydroxy-5-trimethylammoniobenzene) iodide (5). Compound 3 (450 mg, 1.7 mmol) was dissolved in dry MeCN (15 mL) followed by the addition of CH₃I (1.1 mL, 17.3 mmol) to the solution obtained. The mixture was stirred for 20 h and diluted with diethyl ether (15 mL). The precipitate that formed was filtered off and washed with a small amount of diethyl ether to yield a yellow product (500 mg, 72%) with m.p. 206–208 °C, $[\alpha]_D^{25}$ –183 (*c* 0.01 MeOH). ¹H NMR (300 MHz, CD₃OD), δ: 8.64 (s, 2 H, CHN); 7.85 (s, 2 H, Ar, J = 3.3 Hz); 7.61 (s, 2 H, Ar, J = 3.3 Hz); 3.63 (s, 18 H, N(CH₃)₃); 3.59-3.65 (m, 2 H, CH, diaminocyclohexane); 1.93–2.06 (m, 4 H, CH₂, diaminocyclohexane); 1.57-1.86 (m, 4 H, CH₂, diaminocyclohexane); 1.42 (s, 18 H, C(CH₃)₃). ¹³C NMR (300 MHz, CD₃OD), δ: 166.18, 162.94, 141.21, 138.43, 122.76, 121.7, 119.51, 72.83, 58.15, 36.63, 33.83, 29.54, 25.24). Found (%): C, 73.62; H, 9.32; N, 10.66. C₁₉H₂₇NO₆. Calculated (%): C, 73.81; H, 9.29; N, 10.76.

Nickel(II) (1R,2R)-cyclohexane-1,2-diylbis(2-azaethenyl)bis(3-tert-butyl-2-oxybenzene-5-sulfonate) disodium salt (6a). A solution of nickel acetate tetrahydrate (19.9 mg, 80 µmol) in methanol (5 mL) was added to a solution of compound 1 (54.6 mg, 80 µmol) in methanol (1 mL). The solution that was obtained was stirred for 12 h. The precipitate that formed was filtered off and washed with a small amount of cold water and a small amount of cold methanol to yield an orange product $(38 \text{ mg}, 68\%), [\alpha]_D^{25} - 460 (c \ 0.01 \text{ MeOH}).$ ¹H NMR (300 MHz, DMSO-d₆), δ: 7.69 (s, 2 H, C<u>H</u>N); 7.55 (s, 2 H, Ar); 7.4 (s, 2 H, Ar); 3.11 (m, 2 H CH, diaminocyclohexane); 3.3 (m, 4 H, CH₂, diaminocyclohexane); 1.31 (s, 18 H, C(CH₃)₃); 1.25 (m, 4 H, CH₂, diaminocyclohexane). ¹³C NMR (300 MHz, DMSO- d_6), δ: 162.97, 159.02, 138.06, 133.42, 129.08, 127.58, 118.9, 69.66, 35.03, 29.32, 28.2, 23.88. UV (CH₃OH), $\lambda_{max}/nm (\epsilon/L g^{-1} m^{-1})$: 334 (1117); 409 (939). Found (%): C, 48.29; H, 4.98; N, 4.00; Na, 6.57; Ni, 8.4; S, 9.16. C₂₈H₃₄N₂Na₂NiO₈S₂. Calculated (%): C, 48.36; H, 4.93; N, 4.03; Na, 6.61; Ni, 8.44; S, 9.22.

Copper (II) (1*R*,2*R*)-cyclohexane-1,2-diylbis(2-azaethenyl)bis(3-*tert*-butyl-2-oxybenzene-5-sulfonate) disodium salt (6b) was obtained similarly to 6a from compound 1 (54.6 mg, 80 µmol) and copper acetate monohydrate (16 mg, 80 µmol). The yield of violet product 6b was 41 mg (73%), $[\alpha]_D^{25}$ -167 (*c* 0.01 MeOH). UV (CH₃OH), λ_{max} /nm (ϵ /L g⁻¹ m⁻¹): 363 (1408); 573 (61). Found (%): C, 47.97; H, 4.93; Cu, 9.0; N, 3.98; Na, 6.53; S, 9.11. C₂₈H₃₄N₂Na₂CuO₈S₂. Calculated (%): C, 48.03; H, 4.89; Cu, 9.07; N, 4.00; Na, 6.57; S, 9.16.

(1*R*,2*R*)-Cyclohexane-1,2-diylbis(2-azaethenyl)bis(3-*tert*butyl-2-oxy-5-trimethylammoniobenzene)nickel(II) diiodide (7a) was obtained similarly to 6a from compound 5 (64.3 mg, 80 μ mol) and nickel acetate tetrahydrate (19.9 mg, 80 μ mol). The yield of orange product 7a was 57 mg (83%), [α]_D²⁵-326 (*c* 0.01 MeOH). ¹H NMR (300 MHz, DMSO-d₆), δ: 7.94 (d, 2 H, Ar, J = 2.8 Hz); 7.84 (s, 2 H, C<u>H</u>N); 7.47 (d, 2 H, J = 2.7 Hz); 3.54 (s, 18 H, N(CH₃)₃); 3.29 (m, 4 H, C<u>H</u>₂, diaminocyclohexane); 3.2 (s, 2 H, C<u>H</u>, diaminocyclohexane); 1.35 (s, 18 H, C(CH₃)₃); 1.33 (m, 4 H, C<u>H</u>₂, diaminocyclohexane); 1.35 (s, 18 H, C(CH₃)₃); 1.33 (m, 4 H, C<u>H</u>₂, diaminocyclohexane). ¹³C NMR (300 MHz, DMSO-d₆), 8: 162.42, 159.17, 141.15, 133.49, 123.04, 120.9, 119.31, 69.71, 56.28, 35.71, 29.01, 28.38, 23.64. UV (CH₃OH); λ_{max}/nm (ε/L g⁻¹ m⁻¹): 334 (776); 409 (620). Found (%): C, 47.37; H, 6.12; I, 29.33; N, 6.47; Ni, 6.8. C₃₄H₅₂I₂N₄NiO₂. Calculated (%): C, 47.41; H, 6.09; I, 29.47; N, 6.50; Ni, 6.81.

(1*R*,2*R*)-Cyclohexane-1,2-diylbis(2-azaethenyl)bis(3-*tert*butyl-4-oxy-5-trimethylammoniobenzene)copper (II) diiodide (7b) was obtained similarly to **6a** from compound **5** (64.3 mg, 80 µmol) and copper acetate monohydrate (16 mg, 80 µmol). The yield of the violet product was 62 mg (89%), $[\alpha]_D^{25}$ -108 (*c* 0.01 MeOH); UV (CH₃OH), λ_{max} /nm ($\epsilon/L g^{-1} m^{-1}$): 359 (1291), 575 (51). Found (%): C, 46.99; H, 6.10; Cu, 7.3; I, 29.07; N, 6.42. C₃₄H₅₂CuI₂N₄O₂. Calculated (%):C, 47.15; H, 6.05; Cu, 7.34; I, 29.30; N, 6.47.

Nickel(II) (1R,2R)-cyclohexane-1,2-diylbis(2-azaethenyl)bis(3-tert-butyl-2-hydroxy-5-trimethylammoniobenzene)nickel(II) (1R,2R)-cyclohexane-1,2-diylbis(2-azaethenyl)bis(3-tert-butyl-2-oxybenzene-5-sulfonate) (8). A solution of nickel acetate tetrahydrate (10 mg, 40 µmol) in methanol (5 mL) was added to a solution of compound 1 (27.3 mg, 40 µmol) in methanol (1 mL). A solution of nickel acetate tetrahydrate (10 mg, 40 µmol) in methanol (5 mL) was added to a solution of compound 5 (32.2 mg, 40 µmol) in methanol (1 mL). The solutions were stirred for 12 h, and then methanol was added to each solution until precipitates that formed were completely dissolved. Two solutions of thus obtained complexes were mixed, stirred for 12 h, and concentrated to dryness on a rotary evaporator. The dry residue that was obtained was washed on a filter with a small amount of cold water and a small amount of cold methanol to yield an orange product (26 mg, 52%), $[\alpha]_D^{25}$ -478 (c 0.01 DMSO). UV (DMSO), λ_{max} /nm ($\epsilon/L g^{-1} m^{-1}$): 334 (1194), 411 (914). Found (%): C, 59.03; H, 6.94; N, 6.64; Ni, 9.3; S, 5.06 C₆₂H₈₆N₆Ni₂O₁₀S₂. Calculated (%): C, 59.25; H, 6.90; N, 6.69; Ni, 9.34; S, 5.10.

Nickel(II) (1*R*,2*R*)-Cyclohexane-1,2-diylbis(2-azaethenyl)bis-(3-*tert*-butyl-2-oxy-5-trimethylammoniobenzene)copper(II) (1*R*,2*R*)-cyclohexane-1,2-diylbis(2-azaethenyl)bis(3-*tert*-butyl-2-oxybenzene-5-sulfonate) (9). The nickel complex was obtained from compound 1 (27.3 mg, 40 µmol) and nickel acetate tetrahydrate (10 mg, 40 µmol) similarly to complex 8. The copper complex was obtained from compound 5 (32.2 mg, 40 µmol) and copper acetate monohydrate (8 mg, 40 µmol). The yield of the brown product was 26 mg (52%), $[\alpha]_D^{25}$ –308 (*c* 0.01 MeOH). UV (CH₃OH), λ_{max} /nm (ϵ /L g⁻¹ m⁻¹): 357 (1348), 566 (44). Found (%): C, 58.59; H, 6.74; Cu, 5.1; N, 6.70; Ni, 4.7; S, 5.11. C₆₂H₈₆CuN₆NiO₁₀S₂. Calculated (%): C, 59.02; H, 6.87; Cu, 5.04; N, 6.66; Ni, 4.65; S, 5.08.

Copper(II) (1*R*,2*R*)-cyclohexane-1,2-diylbis(2-azaethenyl)bis(3-*tert*-butyl-2-hydroxy-5-trimethylammoniobenzene)nickel(II) (1*R*,2*R*)-cyclohexane-1,2-diylbis(2-azaethenyl)bis(3-*tert*-butyl-2-oxybenzene-5-sulfonate) (10). Nickel complex 10 was obtained from compound 5 (32.2 mg, 40 µmol) and nickel acetate tetrahydrate (10 mg, 40 µmol) similarly to complex 8; the copper complex, from compound 1 (27.3 mg, 40 µmol) and copper acetate monohydrate (8 mg, 40 µmol). The yield of the brown product was 30 mg (59%), $[\alpha]_D^{25}$ –298 (*c* 0.01 MeOH). UV $\begin{array}{l} (CH_{3}OH), \lambda_{max}/nm \ (\epsilon/L \ g^{-1} \ m^{-1}): 360 \ (1189), 563 \ (44). \ Found \ (\%): \\ C, \ 58.78; \ H, \ 6.91; \ Cu, \ 5.0; \ N, \ 6.61; \ Ni, \ 4.6; \ S, \ 5.04. \\ C_{62}H_{86}CuN_{6}NiO_{10}S_{2}. \ Calculated \ (\%): \ C, \ 59.02; \ H, \ 6.87; \ Cu, \ 5.04; \ N, \ 6.66; \ Ni, \ 4.65; \ S, \ 5.08. \end{array}$

Copper(11) (1*R*,2*R*)-cyclohexane-1,2-diylbis(2-azaethenyl)bis(3-*tert*-butyl-2-oxy-5-trimethylammoniobenzene)copper(11) (1*R*,2*R*)-cyclohexane-1,2-diylbis(2-azaethenyl)bis(3-*tert*-butyl-2-oxybenzene-5-sulfonate) (11). The first copper complex 11 was obtained similarly to complex 8 from compound 1 (27.3 mg, 40 µmol) and copper acetate monohydrate (8 mg, 40 µmol). The second copper complex was obtained from compound 5 (32.2 mg, 40 µmol) and copper acetate monohydrate (8 mg, 40 µmol). The yield of the violet product was 30 mg (59%), $[\alpha]_D^{25}$ -136 (*c* 0.01 MeOH). UV (CH₃OH), λ_{max} /nm (ϵ //L g⁻¹ m⁻¹): 362 (1555), 573 (61). Found (%): C, 58.55; H, 6.89; Cu, 9.9; N, 6.58; S, 5.02. C₆₂H₈₆Cu₂N₆O₁₀S₂. Calculated (%): C, 58.79; H, 6.84; Cu, 10.03; N, 6.64; S, 5.06.

References

- W. Zhang, J. L. Loebach, S. R. Wilson, E. N. Jacobsen, J. Am. Chem. Soc., 1990, 112, 2801.
- R. Irie, K. Noda, Y. Ito, N. Matsumoto, T. Katsuki, *Tetra-hedron Lett.*, 1990, **31**, 7345.
- 3. M. Hayashi, H. Kaneda, N. Oguni, *Tetrahedron: Asymmetry*, 1995, **10**, 2511.
- 4. J. F. Larrow, E. N. Jacobsen, J. Org. Chem., 1994, 59, 1939.
- G. M. Sammis, H. Danjo, E. N. Jacobsen, J. Am. Chem. Soc., 2004, 126, 9928.
- Y. N. Belokon', B. Green, N. S. Ikonnikov, V. S. Larichev, B. V. Lokshin, M. A. Moskalenko, M. North, C. Orizu, A. S. Peregudov, G. I. Timofeeva, *Eur. J. Org. Chem.*, 2000, 14, 2655.
- Y. N. Belokon, D. Chusov, D. A. Borkin, L. V. Yashkina, P. Bolotov, T. Skrupskaya, M. North, *Tetrahedron: Asymmetry*, 2008, **19**, 459.
- Z. Chen, M. Furutachi, Y. Kato, S. Matsunaga, M. Shibasaki, *Angew. Chem.*, *Int. Ed.*, 2009, 48, 2218.
- 9. C. Mazet, E. N. Jacobsen, Angew. Chem., Int. Ed., 2008, 47, 1762.
- 10. D. E. White, E. N. Jacobsen, *Tetrahedron: Asymmetry*, 2003, **14**, 3633.
- 11. S. Mouri, Z. Chen, H. Mitsunuma, M. Furutachi, S. Matsunaga, M. Shibasaki, J. Am. Chem. Soc., 2010, 132, 1255.
- Z. Zhang, Z. Wang, R. Zhang, K. Ding, *Angew. Chem.*, 2010, 122, 6898.
- J. Park, K. Lang, K. A. Abboud, S. Hong, J. Am. Chem. Soc., 2008, 130, 16484.
- 14. S. Handa, K. Nagawa, Y. Sohtome, M. S. Matsunaga, M. Shibasaki, *Angew. Chem.*, *Int. Ed.*, 2008, **47**, 3230.
- Y. N. Belokon, W. Clegg, R. W. Harrington, M. North, C. Young, *Inorg. Chem.*, 2008, 47, 3801.
- 16. J. Sun, F. Yuan, M. Yang, Y. Pan, C. Zhu, *Tetrahedron Lett.*, 2009, **50**, 548.
- A. M. Castilla, S. Curreli, E. C. Escudero-Adán, M. Martínez Belmonte, J. Benet-Buchholz, A. W. Kleij, *Org. Lett.*, 2009, 11, 5218.
- M. S. Matsunaga, J. Das, J. Roels, E. M. Vogl, N. Yamamoto, T. Iida, K. Yamaguchi, and M. Shibasaki, *J. Am. Chem. Soc.*, 2000, **122**, 2252.

- 19. S. Liao, B. List, Angew. Chem., Int. Ed., 2010, 49, 628.
- 20. C. Baleizo, H. Garcia, Chem. Rev., 2006, 106, 3987.
- 21. R. M. Haak, S. J. Wezenberg, A. W. Kleij, *Chem. Commun.*, 2010, **46**, 2713.
- 22. B. M. Choudary, T. Ramani, H. Maheswaran, L. Prashant, K. V. S. Ranganath, K. V. Kumar, *Adv. Synth. Catal.*, 2006, 348, 493.
- 23. S. D. Bella, G. Consiglio, N. Leonardi, S. Failla, P. Finocchiaro, I. Fragala, *Eur. J. Inorg. Chem.*, 2004, **13**, 2701.
- 24. J. F. Larrow, E. N. Jacobsen, Y. Gao, Y. Hong, X. Nie, C. M. Zepp, J. Org. Chem., 1994, 59, 1939.
- 25. F. Galsbøl, P. Steenbøl, B. S. Sørensen, Acta Chem. Scand., 1972, 26, 3605.
- 26. M. Braun, R. Fleischer, B. Mai, M.-A. Schneider, S. Lachenicht, *Adv. Synth. Catal.*, 2004, **346**, 474.
- G. M. Sheldrick, SADABS, v. 2.03, Bruker/Siemens Area Detector Absorption Correction Program, Bruker AXS, Madison, Wisconsin, USA, 2003.
- 28. A. L. Spek, *PLATON, A Multipurpose Crystallographic Tool*, Utrecht University, Netherlands, 1998.
- 29. G.M. Sheldrick, Acta Cryst., 2008, A64, 112.

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