

# Synthesis of Chelating Polymer Sorbents by Using the $S_N^H$ Methodology

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**ABSTRACT:** The article describes a new synthetic approach to modify the structure of phenol-formaldehyde and resorcinol-formaldehyde resins, which enables one to functionalize a polymer matrix by using the  $S_N^H$  (nucleophilic aromatic substitution of hydrogen) methodology. Direct heteroarylation of phenol (resorcinol) fragments in polymer chains with 1,2,4-triazine derivatives illustrates a new synthetic method in the polymer chemistry. The feature of this methodology is that it provides an opportunity to accomplish direct one-pot polymer transformations by incorporating of rather complicated chelating groups through the displacement of hydrogen in phenol moieties. It has been shown that in order to obtain chemically modified polymers on the basis of phenol-formaldehyde and resorcinol-formaldehyde resins with a high degree of sub-

stitution with chelating units, a polymer matrix has to react with 3-(pyridin-2'-yl)-1,2,4-triazin-5(2H)-one. Also, it has been found that polymer sorbents with a high selectivity can be obtained by using the template method. Targeted synthesis of model compounds, as structural units of the chelating polymers, and elucidation of the structure of their complexes with copper (II) ions have shown that the most plausible type of coordination is formation of the bridge 1 : 1 complexes of the  $\alpha,\alpha'$ -bipyridinyl type. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 1970–1978, 2012

**Key words:** functionalization of polymers;  $S_N^H$  methodology; phenol-; and resorcinol-formaldehyde resins; chelating ion exchangers; X-ray

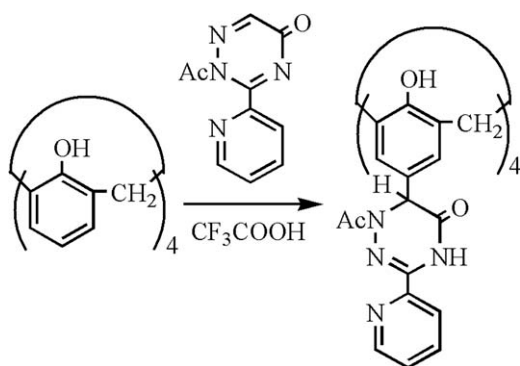
## INTRODUCTION

Development of a new technology for separation and recovery of non-ferrous metals (NFM) is an actual task, related to obtaining of new sorption materials exhibiting advanced selectivity characteristics. A classical method to obtain polymer sorbents which are sensitive towards NFM ions is based on using a polymer matrix bearing chelating functional groups.<sup>1</sup> In order to obtain such resins, a polymer matrix should have rather reactive functional groups, which enable one to functionalize a polymer structure by incorporating bi- and polydentate chelating groups.<sup>2</sup> Unfortunately, a number of synthetic approaches to realize chemical modification of polymers by incorporating of chelating units appear to be quite limited.

During the last two decades, the methodology of nucleophilic aromatic substitution of hydrogen ( $S_N^H$ ) has become an effective synthetic tool to modify a great deal of aromatic compounds. In these cross-coupling reactions (not catalyzed by metals) the formation of C–C, C–N, C–O, C–P, C–S, C–Si, and

other chemical bonds between a  $\pi$ -deficient arene moiety and a nucleophile takes place.<sup>3–5</sup> One advantage of the  $S_N^H$  reactions, proceeding (like traditional  $S_N^{ipso}$  substitution reactions) according to the two-steps scheme (addition–oxidation)  $S_N^H$  (AO), is the absence of any by-products, besides water. In a number of cases the process can be stopped at the first stage, thus affording relatively stable  $A_N$  adducts. A great variety of nucleophiles have already been used in the  $S_N^H$  reactions, both anionic ones and those bearing a fractional negative charge. For instance, phenols, their ethers, and macrocyclic derivatives, such as benzocrowns<sup>6</sup> and calixarenes, have been exploited as nucleophiles (Scheme 1). Due to incorporation of 3-(pyridinyl-2')-1,2,4-triazin-5-one chelating groups, which are structurally similar to  $\alpha,\alpha'$ -bipyridinyl, modified calixarenes proved to exhibit an enhanced receptor ability towards  $Ca^{2+}$  and  $Mg^{2+}$  ions.<sup>7</sup> Detailed study on liquid extraction of  $Cu^{2+}$ ,  $Ag^+$ ,  $Fe^{3+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$  ions with calixarenes in which resorcinol fragments were modified with 1,2,4-triazin-5-one residues has demonstrated, that these compounds can be effectively used for selective extraction of copper (II) from a mixture of ions.<sup>8</sup> We have previously reported on the fact that the  $S_N^H$  methodology might be useful in the chemistry of polymers for heterylation of phenol-formaldehyde resins, which can be regarded as multi-centered

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**Scheme 1** Modification of calyx[4]arene with 3-(pyridin-2'-yl)-1,2,4-triazin-5(2H)-one.

polymeric nucleophilic agent. Indeed, the reaction of the latter with electrophilic 3-(pyridinyl-2')-1,2,4-triazin-5-one results in the formation of a new polymer bearing the chelating groups, which are structurally similar to  $\alpha,\alpha'$ -bipyridinyl, the key fragment in a number of polymeric sorbents.<sup>9</sup>

This article is dedicated to further development of the  $S_N^H$  methodology for polymer transformations of resorcinol-formaldehyde resins, elucidation of sorption characteristics for the modified polymers, and coordination structure of the chelating unit on the basis of model low-molecular weight compounds.

## MATERIALS AND METHODS

### Material

Phenol-formaldehyde (1) and resorcinol-formaldehyde (2) resins of linear structure were obtained according to the previously described procedure.<sup>10</sup> All other reagents were used without additional purification. Elemental analyses were carried out on automatic analyzer (Perkin-Elmer, USA). FTIR spectra were recorded on "Spectrum One" FTIR spectrometer (Perkin-Elmer), using the Diffuse Reflectance Sampling Accessory (DRA). NMR  $^1H$  spectra for low-molecular compounds and polymers were recorded on (Bruker, Germany) DRX-400 spectrometer.

### Polymer-analogous transformations

#### Modification of polymers with 1,2,4-triazine derivatives

Novolac was functionalized with 6-phenyl-2-ethyl-1,2,4-triazine-4-oxide (3) and 3-(pyridin-2'-yl)-1,2,4-triazine-5(2H)-one (4), as described in work,<sup>8</sup> to give polymers with the degree of substitution (DS) 20 (5) and 75% (6), correspondingly. Resorcinol-formaldehyde resin was modified in the following way:

1. 3-(Pyridin-2'-yl)-1,2,4-triazine-5(2H)-one (4) in the quantity of 0.3 g (1.7 mmol) was placed in

10-mL flask, 1.5 mL of acetic anhydride was added and the reaction mixture was refluxed for 10 min. The reaction mixture was cooled up to  $-20^\circ C$  and the precipitate obtained was filtered off. To this solid material 3 mL of chloroform and 1.5 mL (23 mmol) of trifluoroacetic acid were added, after that the mixture was treated with 0.23 g (1.7 mmol) of resorcinol-formaldehyde resin. The reaction mixture was kept on reflux for 4 h, and evaporated to dryness under vacuum. Dry residue was treated with 14 mL of diethyl ether and stirred for 30 min to give a precipitate. Liquid fraction was decanted, while solid was treated with aqueous solution of  $NaHCO_3$  (5.7 g per 100 mL of water) and stirred for 24 h. The precipitate was filtered, washed with water, and dried at  $50^\circ C$  until constant weight. Yield 0.4 g. Analysis calculated for  $(C_{12}H_9O_4)(C_6H_4O_2)_8(C_{10}H_9N_3O_2)$ : C, 62.51; H, 6.27; N, 4.28. Found: C, 62.28; H, 5.93; N, 4.16. Substitution degree is 15% (7).

2. Another experiment was carried out under similar conditions with the difference that a mixture of starting materials was kept for 24 h at room temperature to allow the resin to swell. Yield 0.45 g. Analysis calculated for the substitution degree 50% (8): C, 61.72; H, 6.08; N, 4.68. Found: C, 61.57; H, 5.84; N, 4.83.

Cross-linked polymers (sorbents) (9) on the basis of novolac resin, modified with 3-(pyridin-2'-yl)-1,2,4-triazine-5(2H)-one

Modification of novolac was carried out in the manner described above. After reflux of the starting materials for 4 h, a solution of 2.54 g (63 mmol) of  $NaOH$  in 5 mL of water was added, followed by the addition of 0.31 g (1.61 mmol) of  $Cu(AcO)_2 \cdot H_2O$  in 5 mL of water. The solution obtained was dried on rotary evaporator, and after treatment with 1.96 g (14 mmol) of urotropin the reaction mixture was heated up to  $175^\circ C$  gradually at heating speed  $5^\circ$  per min. The residue was washed with 300 mL of water, dried at  $70^\circ C$  up to a constant weight. Yield 0.5 g. Analysis calculated for  $[(C_{55}H_{25}O_8)(C_{10}H_9N_4O_2)_6]_2(CH_2)_8 \cdot Cu_{15}$  (9): C, 54.53; H, 3.35; N, 12.82; Cu, 18.31. Found: C, 54.19; H, 3.15; N, 12.45; Cu, 18.85.

The obtained copper (II) complex of cross-linked polymer 9 (0.2 g) was washed with 6.5% of aqueous ammonia solution  $5 \times 16$  mL until negative test for copper (II) ions in waste solutions was obtained. The residue was washed with 50 mL of water, and dried at  $70^\circ C$  up to a constant weight. According to elemental analysis (EA) data the content of copper proved to be 15.99%.

In the other experiment, the copper complex of cross-linked polymer **9** was washed with 5% solution of trilon (5 × 300 mL) up to a negative test for copper (II) ions in waste solutions. The residue was washed in 50 mL of water, and dried at 70°C up to a constant weight. EA gave the copper content 4.73%.

#### Polycondensation of 1-acetyl-3-(pyridin-2'-yl)-6-(4'-hydroxyphenyl)-1,2,4-triazine-5(2H)-one (**10**) with formaldehyde

Phenol was functionalized with 3-(pyridin-2'-yl)-1,2,4-triazine-5(2H)-one according to work.<sup>11</sup> The obtained product **10** was subjected to polycondensation in the following way:

Compound **10** (0.37 g, 1.45 mmol) was placed in 10-mL flask, mixed with paraform (0.04 g, 1.45 mmol) and oxalic acid (0.01 g) and heated up to 100°C for 1 h. Reaction mixture was cooled to a room temperature, washed with water and dried *in vacuo*. Yield 0.35 g. The analysis by <sup>1</sup>H-NMR spectroscopy revealed the presence of the starting materials in the obtained product.

#### Synthesis of model compounds

##### 1-Acetyl-3-(pyridin-2'-yl)-6-(3',5'-dimethyl-4'-hydroxyphenyl)-1,2,4-triazine-5(2H)-one (**11**)

A mixture of 0.5 g (2.88 mmol) 3-(pyridin-2'-yl)-1,2,4-triazine-5(2H)-one and 2.5 mL of acetic anhydride was kept on reflux for 10 min. The reaction mixture was cooled down to -20°C and the precipitate obtained was separated by filtration. The solid (0.83 g) was added into a mixture of 21 mL of chloroform and 10 mL of trifluoroacetic acid. The reaction mixture was kept on reflux for 4 h and then evaporated *in vacuo* to dryness. The residue was washed with water up to neutral pH, filtered and dried at 60°C. Yield 0.78 g (89%). Analysis calculated for C<sub>18</sub>H<sub>19</sub>N<sub>4</sub>O<sub>2</sub>: C, 62.44; H, 5.19; N, 16.17. Found: C, 62.33; H, 5.37; N, 15.87.

##### Copper (II) complex of 1-acetyl-3-(pyridin-2'-yl)-6-(3',5'-dimethyl-4'-hydroxyphenyl)-1,2,4-triazine-5(2H)-one (**12**)

Compound **11** (0.375 g, 1.1 mmol) was dissolved in 10 mL of water, containing 0.089 g (2.2 mmol) of NaOH and treated with 0.22 g (1.1 mmol) of Cu(AcO)<sub>2</sub>·H<sub>2</sub>O. The precipitate obtained was filtered off and recrystallized from acetic acid. Yield 0.14 g (33%). Analysis calculated for C<sub>16</sub>H<sub>18</sub>N<sub>3</sub>O<sub>3</sub>Cu (CH<sub>3</sub>COO)(OH): C, 54.53; H, 3.35; N, 12.82; Cu, 18.31. Found: C, 54.19; H, 3.15; N, 12.45; Cu, 18.85.

##### 3-(Pyridin-2'-yl)-6-(3',5'-dimethyl-2'-hydroxyphenyl)-1,2,4-triazine-5(2H)-one (**13**)

Air was bubbled for 30 h through a mixture of 0.45 g (2.6 mmol) 3-(pyridin-2'-yl)-1,2,4-triazine-5(2H)-

one, 18 mL of trifluoroacetic acid, and 0.32 mL (2.6 mmol) of 2,4-dimethylphenol. The reaction mixture was evaporated to dryness and treated with 5 mL of water. The solid was washed with 3 × 5 mL water, dried *in vacuo* and recrystallized from acetonitrile. Yield 0.21 g (27%). M.p. 245–246°C. Analysis calculated for C<sub>16</sub>H<sub>14</sub>N<sub>4</sub>O<sub>2</sub>: C, 65.31; H, 4.76; N, 19.05. Found: C, 65.45; H, 4.94; N, 19.36. 400 MHz NMR <sup>1</sup>H (DMSO-*d*<sub>6</sub>), δ, ppm: 8.85 (d, 1H Py); 8.38 (d, 1H Py), 8.13 (m, 1H Py), 7.75 (m, 1H Py), 7.48 (s, 1H Ar), 7.10 (s, 1H Ar), 2.21 (d, 6H CH<sub>3</sub>).

##### Copper complex of 3-(pyridin-2'-yl)-6-(3',5'-dimethyl-2'-hydroxyphenyl)-1,2,4-triazine-5(2H)-one (**14**)

Compound **13** (0.1 g, 0.34 mmol) was dissolved in 10 mL of water, containing 0.054 g (1.36 mmol) of NaOH and treated with 0.136 g (0.68 mmol) of Cu(AcO)<sub>2</sub>·H<sub>2</sub>O. The precipitate obtained was filtered off and recrystallized from acetic acid. Analysis calculated for C<sub>16</sub>H<sub>13</sub>N<sub>4</sub>O<sub>2</sub>Cu(CH<sub>3</sub>COO)(OH): C, 49.76; H, 3.91; N, 12.90; Cu, 14.74. Found: C, 49.83; H, 3.67; N, 12.65; Cu, 14.85.

#### Sorption properties of modified resins

Sorption properties were studied by stirring of polymer (0.1 g) in 8.0 mL of a standard test solution (0.025M solution of copper (II), nickel (II), cobalt (II), and zinc (II) acetates in 1M ammonia-acetate buffer, pH = 6.5) for 4 h; after that it was kept under ambient conditions for 20 h. Sorption capacity was calculated as the difference between initial and equilibrium concentrations of a metal in the solution, determined by the method of atomic absorption spectroscopy (Soolar M6, Thermo, USA). Relative error for all metal measurements was within ±0.08%.

#### X-ray diffraction analysis

X-ray analyses of compounds **11** and **12** were carried out on automatic monocrystal diffractometer "Xcalibur 3" (CCD detector, MoK<sub>α</sub>, graphite monochromator). The structure has been deciphered directly and specified by the entire matrix least-squares method (LSM) in anisotropic approximation for non-hydrogen atoms, using the programs SHELX-97.<sup>12</sup> Crystallographic data for the structures **11** and **12** are summarized in Table I. These data have been deposited with the Cambridge Crystallographic Data Centre (12 Union Road, Cambridge CB2 1EZ, U.K.; fax (+44) 1223-336-033 or deposit@ccdc.cam.ac.uk) and may be obtained free of charge from [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html). The reference numbers are 260575-260577.



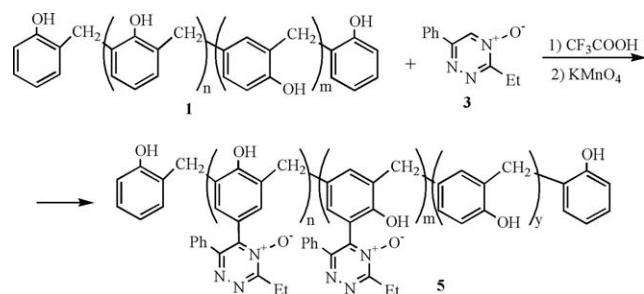
TABLE I  
X-Ray Crystallography Data for 11 and 12

Structure	11	12
Chemical formula	$C_{18}H_{18}N_4O_3$	$C_{20}H_{22}CuN_4O_6$
Mol. Wt.	338.36	477.96
Cryst. syst.	Tetragonal	Monoclinic
Space group	$I4_1/a$	$P2_1/c$
$a, b, c$ (Å)	25.9880(14), 25.9880(14), 10.2611(9)	14.1281(11), 16.1428(14), 9.4758(6)
$\beta$ (deg)	90.00	96.038(6)
$V$ (Å <sup>3</sup> )	6930.1(8)	2149.1(3)
$Z$	16	4
$D_{\text{calcd}}$ (g cm <sup>-3</sup> )	1.297	1.477
$\mu$ (Mo $K_\alpha$ ) (mm <sup>-1</sup> )	0.091	1.060
Crystal size (mm)	$0.51 \times 0.33 \times$ 0.19	$0.136 \times 0.064 \times$ 0.015
$T$ (K)	295(2)	295(2)
Reflections measured, unique reflections	9306, 3498	10085, 4243
Obsd data [ $I > 2\sigma(I)$ ]	1492	2230
$R(F)$ [ $I > 2\sigma(I)$ ]	0.0449	0.0396
$wR(F_2)$	0.0698	0.0463
$S$	1.005	1.006
$\Delta\rho_{\text{min}}, \Delta\rho_{\text{max}}$ (e Å <sup>-3</sup> )	-0.225/0.285	-0.361/0.437

## RESULTS AND DISCUSSION

### Synthesis of chelating polymers

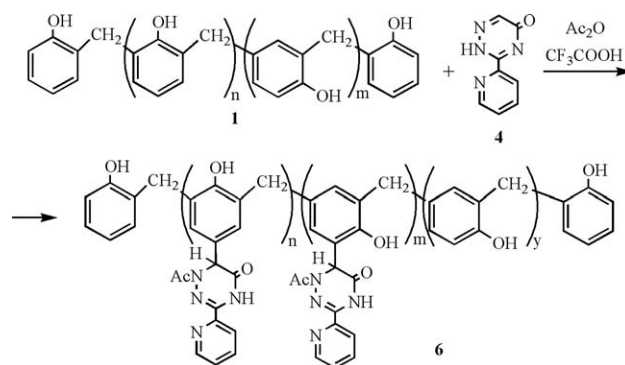
For the first time novolac **1** has been involved into the reaction with 6-phenyl-2-ethyl-1,2,4-triazine-4-oxide (Scheme 2) in methylene chloride in the presence of trifluoroacetic acid.<sup>13</sup> In the course of this reaction the C—C cross-coupling takes place resulting in the formation of resin with the temperature softening 140–148°C. This resin can be regarded as product of nucleophilic substitution of hydrogen in the heterocyclic units, or as that of electrophilic substitution of hydrogen in phenol fragments. The fact of covalent C—C bond formation has been substantiated by analytical data: (i) EA has shown no changes in the composition after many hours hot extraction with acetone; (ii) a difference between FTIR-spectra **1** and **5** indicates the presence of absorption band at 1370 cm<sup>-1</sup>, which is characteristic for the starting 1,2,4-triazine *N*-oxide; and (iii) the <sup>1</sup>H-NMR spectra demonstrate decrease in a number of aromatic protons.



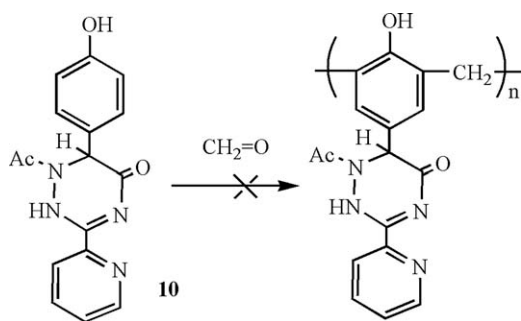
Scheme 2 Modification of novolac with 6-phenyl-2-ethyl-1,2,4-triazin-4-oxide.

The analytical data also indicate that conversion in the reaction 6-phenyl-2-ethyl-1,2,4-triazin-4-oxide is small and does not exceed 20%. In other words, even phenol fragments, having free *para*-positions do not react fully with this 1,2,4-triazin-4-oxide. Taking into account the fact that in electrophilic substitution reactions in the series of phenols the ratio of *para*- and *ortho*-isomeric products (2- and 4-substitution) is approximately 10 : 1,<sup>11</sup> a number of groups capable of chelating does (fragments (*m*) in **5**) scarcely exceed 2%.

A higher reactivity has been demonstrated by 3-(pyridin-2'-yl)-1,2,4-triazin-5(2*H*)-one (Scheme 3). The reaction of preliminary acetylated triazinone **4** with **1** on heating in chloroform afforded compound **6** with temperature of softening 230–240°C. Unreacted 1,2,4-triazin-5(2*H*)-one was eliminated by extraction with hot acetone. The difference of FTIR spectra of **1** and **6** shows absorption band at 1716 cm<sup>-1</sup>, which is characteristic for lactams and is absent in the starting 2-acetyl-3-(2-pyridyl)-1,2,4-triazin-5(2*H*)-one. Like in case with the resin **5**, decrease in number of aromatic protons in the <sup>1</sup>H-NMR spectrum of **6** relative to that for compound **1** is in agreement with the C—C bond formation. Besides that, in the in the <sup>1</sup>H-NMR spectra of the modified polymer the resonance signal of the acetyl groups (singlet at 2.01 ppm), the characteristic signal of the C(*sp*<sup>3</sup>)-H protons (singlet at 5.90 ppm), multiplets of aromatic protons in the range 6.0–7.1 ppm (polymer backbone), and 7.1–8.6 ppm [1-acetyl-3-(pyridin-2'-yl)-1,2,4-triazin-5(2*H*)-one fragments] are available.<sup>6–8</sup> It follows from the EA data that the  $A_N$  addition process is realized at approximately 75%. For polymer **6** a number of groups capable of chelating is not depending on reactivity of *para*- and *ortho*-positions, since it is determined entirely by the pyridinyl-triazine fragment, similar to  $\alpha, \alpha'$ -bipyridyl. Thus, novolac can be modified with 3-(pyridin-2'-yl)-1,2,4-triazin-5(2*H*)-one (**4**) much more easily, than with 6-phenyl-2-ethyl-1,2,4-triazin-4-oxide (**3**).



Scheme 3 Modification of novolac with 3-(pyridin-2'-yl)-1,2,4-triazin-5(2*H*)-one.

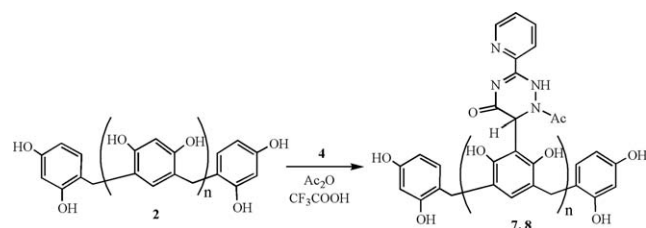


**Scheme 4** Polycondensation of 1-acetyl-3-(pyridin-2'-yl)-6-(4-hydroxyphenyl)-1,2,4-triazin-5(2H)-one (**10**) with formaldehyde.

Attempts to prepare a regularly substituted novolac with 100% substitution degree have been undertaken by means of polycondensation of 1-acetyl-3-(pyridin-2'-yl)-6-(4'-hydroxyphenyl)-1,2,4-triazin-5(2H)-one (**10**) with formaldehyde (Scheme 4). Monomer **10** was obtained, but subsequent condensation with formaldehyde has failed, apparently, due to a very low reactivity of substituted phenol.

According to well-known data on reactivity of monomers, resorcinol-formaldehyde resins (**2**) appear to have more reactive nucleophilic centers, than novolac. However, the treatment of **2** with 3-(pyridin-2'-yl)-1,2,4-triazin-5(2H)-one (Scheme 5) gave product **7** with substitution degree only 15%, as indicated by  $^1\text{H-NMR}$ . Preliminary swelling of polymer **2**, followed by the reaction with triazinone **10** afforded the polymer **8** with substitution degree 50%. The  $^1\text{H-NMR}$  spectra of modified polymer **8** are in full agreement with the structure, exhibiting new signals of acetyl groups (a singlet at 2.00 ppm) and for the  $\text{C}(\text{sp}^3)\text{-H}$  proton resonances (a singlet at 6.05 ppm), as well as aromatic protons of resorcinol-formaldehyde resins (polymer backbone) in the range of 5.8–7.1 ppm and the fragments of 1-acetyl-3-(pyridine-2'-yl)-1,2,4-triazin-5(2H)-one (pendant groups) in the range of 7.1–8.6 ppm.

Thus, resorcinol-formaldehyde resins exhibit a less reactivity in the nucleophilic addition reaction on the triazine ring of 1-acetyl-3-(pyridin-2'-yl)-1,2,4-triazin-5(2H)-one, than their phenol analogues.



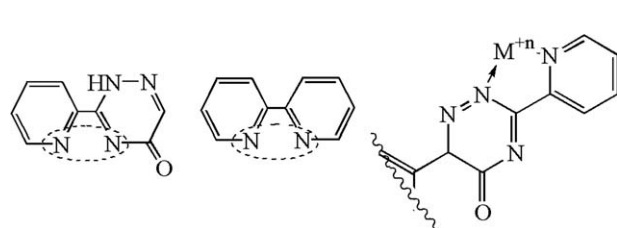
**Scheme 5** Modification of resorcinol-formaldehyde resin with 3-(pyridin-2'-yl)-1,2,4-triazin-5(2H)-one.

### Sorption properties of modified resins

Since modified resins mentioned above contain the chelating group, which is able to provide coordination of the  $\alpha,\alpha'$ -bipyridinyl type (Scheme 6), the synthesized polymers are chelating ones and are expected to demonstrate sorption properties toward metal ions. We have studied their sorption abilities toward the Irving-Williams line ions ( $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Co}^{2+}$ ) for 24 h at  $\text{pH} = 6.5$ , i.e., under conditions in which modified resins are insoluble in water (Table II). It can be seen from Table II that the resin modified with *N*-oxide **3** exhibits 100% selectivity towards copper (II) ions, but it has a low capacity. Use of 3-(pyridin-2'-yl)-1,2,4-triazin-5(2H)-one **4** enhances total capacity of the resin, but its selectivity toward copper (II) ions becomes a lower one. This fact can be explained by a higher degree of polymer modification in case of **6**, and the formation of chelating rings of the  $\alpha,\alpha'$ -bipyridinyl type, which is excepted for resin **5**. Product **6** possesses a low static sorption capacity toward metal ions and a good selectivity toward copper (II) ions. According to theoretical estimations, the obtained polymer is able to absorb relevant metals in concentrations up to  $1.5 \text{ mmol g}^{-1}$ , which exceed 10-times the real static sorption capacity, i.e., only 8–10% of groups, capable of complex formation, are involved in the process of sorption. It can be attributed to the specific arrangement of acidic (phenol fragments) and coordinating (pyridine and triazine rings) groups, or a low spatial accessibility of chelating fragments, since only two types of complexes can be formed principally (Scheme 7).

Use of resorcinol-formaldehyde resins, as a polymeric matrix, enhances their capacities due to additional phenol hydroxides appear to be involved in the coordination. Besides that, the greater the DS, the greater the capacity. However, an increase in capacity results in a reduced sorption selectivity towards copper (II) ions, which is a common feature of the process.

Template synthesis of sorbent has also been performed in order to increase the capacity characteristics of resin **6**. A water-soluble copper (II) complex of polymer **6** has first been obtained under homogeneous conditions [polymer was dissolved in aqueous



**Scheme 6** Formation of the chelate ring of the  $\alpha,\alpha'$ -bipyridinyl type.

TABLE II  
Sorption Capacity of Modified Phenol-Formaldehyde (5, 6) and Resorcinol-Formaldehyde Resins (7, 8)

Sorbent	Degree of substitution (%)	Sorption capacity (selectivity) mmol/g (% from SEC)				
		Cu <sup>2+</sup>	Ni <sup>2+</sup>	Zn <sup>2+</sup>	Co <sup>2+</sup>	SEC
5	20	0.074 (100)	0	0	0	0.074
6	75	0.097 (83)	0.018 (15)	0.002 (2)	0	0.117
7	15	0.356 (58)	0.087 (14)	0.080 (13)	0.088 (15)	0.611
8	50	0.388 (41)	0.181 (19)	0.179 (19)	0.193 (21)	0.941

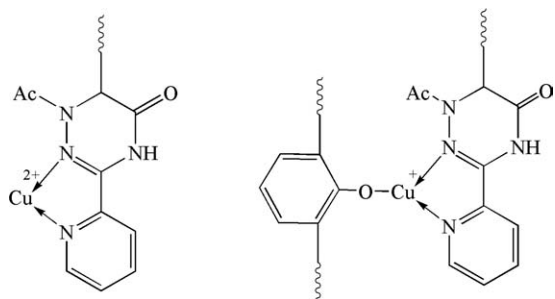
NaOH, then treated with Cu(OCOCH<sub>3</sub>)<sub>2</sub> and the product was precipitated with acetone]. Then it was subjected to cross-linking with formaldehyde; after that the copper (II) ions was scoured with complexing agents, such as trilon or an aqueous ammonia solution (Scheme 8).

The data of elemental analyses show that it is better to scour the copper (II) ions with trilon, although some amount of metal still remains in the polymer, which cannot be removed due to a strong molecular cross-linking. Moreover, in the FTIR-spectrum of the resin treated with trilon, the band at 1705 cm<sup>-1</sup> is still available, thus indicating the presence of residual trilon, i.e., the complex which is formed during the washing procedure is attached partly to a polymer matrix.

Sorption characteristics of resins, obtained by the template method are given in Table III. They show that the template synthesis enhances the sorption capacity up to 23% (ammonia treatment) and 11% (trilon treatment) from theoretical value, providing a high selectivity (98–100%), in spite of the fact the degree of elimination of copper (II) ions remains 15% on use of ammonia and 75%—in case of trilon.

#### Study on coordination units structure in chelating polymers obtained

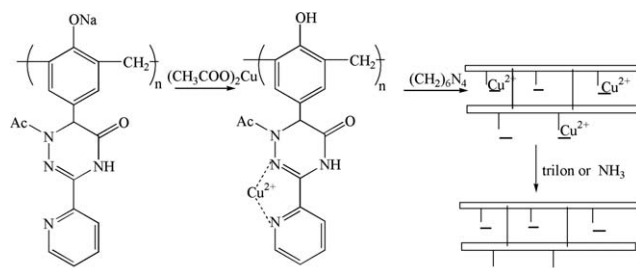
In order to establish the structure of coordination units formed in the process of ions sorption, model compounds, such as 1-acetyl-3-(pyridin-2'-yl)-6-(3',5'-dimethyl-4'-hydroxyphenyl)-1,2,4-triazin-5(2H)-one (**11**), imitating part of the polymer chain **6**, and copper(II) complex **12** (Scheme 9) have been obtained. The data



Scheme 7 Two types of complexes are possible basically in product **4**.

of X-ray analyses of these compounds are presented in Table II and Figures 1 and 2. Compound **11**, the so-called  $\sigma^H$ -adduct, is an example of the key intermediates of  $S_N^H$ -reactions. Actually, C-6 carbon of the triazine ring (Fig. 1) has the tetrahedral structure with slight discrepancy of bond angles values (2–3°) from those for the  $sp^3$ -hybridized carbon. Moreover, C6—C bond is longer than that of carbon-carbon bonds of an aromatic system (Table IV). A similar  $\sigma^H$ -adduct derived from the reaction of 1,2,4-triazin-*N*-oxide with indole has been elucidated by X-ray crystallography.<sup>14</sup> In case of compound **11** the dihydro-1,2,4-triazine fragment is not planar and has the “envelope” conformation: H3 atom occupies the pseudoequatorial position, while 2,6-dimethylphenol fragment is in the pseudoaxial position (Fig. 1). Analysis of the shortened O...O contacts shows that the crystalline structure **11** is stabilized by intramolecular hydrogen bonds between the hydroxy group of phenol moieties and the carbonyl group of the triazine ring with the O...O distance of 2.82 Å.

Structural elucidation of the complex **12** has shown that besides one molecule of the ligand, the acetate and hydroxide ions are involved. Thus, only one chelating ring is formed in the complex by coordinating with nitrogen atoms of pyridine and triazine rings. Contrary to expectations, the hydroxy group of phenol fragments does not participate in complexing. The complex basic unit **12** is described by the formula: [Cu(L)(H<sub>2</sub>O)(CH<sub>3</sub>COO)]. Copper (II) ion forms a coordination environment with the square-pyramidal geometry in the crystal. Oxygen atoms of water and the acetate group, as well as nitrogen atoms of the pyridine and triazine rings form the basis of pyramid, while the carbonyl



Scheme 8 Template synthesis of sorbent.



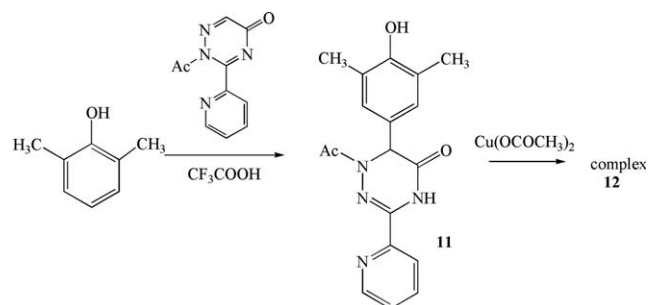
**TABLE III**  
Sorption Capacity of Novolac Resins 6, Prepared by Template Synthesis

Method of copper ions removal	Sorption capacity (selectivity) mmol/g (% from SEC)				SEC
	Cu <sup>2+</sup>	Co <sup>2+</sup>	Ni <sup>2+</sup>	Zn <sup>2+</sup>	
Trilon	0.165(100)	0	0	0	0.165
Aqua Ammonia	0.335(98)	0	0.007(2)	0	0.342

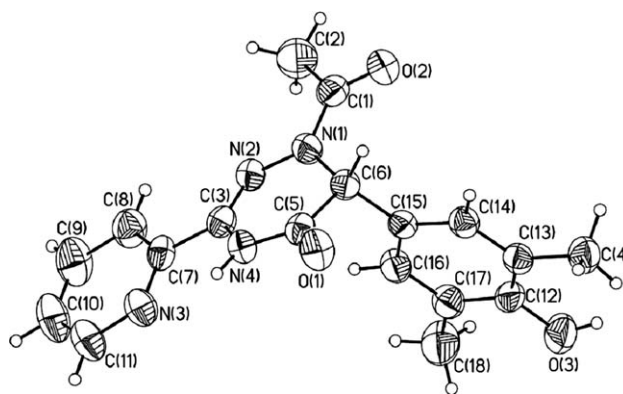
oxygen of the acetate ion of a neighboring molecule is on the top of pyramid (Figs. 2 and 3). Thus, the acetate ion plays the bidentate bridge function to form the coordinated polymer chain in the crystal. Again, the shortened O...O contacts indicate that the crystal structure is stabilized by hydrogen bonds, both between molecular complexes, and also inside of the complex. Intramolecular hydrogen bonds are formed due to water hydrogen atoms which are linked with carbonyl groups of the acetate ion and 1,2,4-triazin-5-one with the O...O distances of 2.56 and 2.62 Å, correspondingly. Stabilization of the crystal structure is realized through hydrogen bonds between coordinated polymer chains, which are formed by interacting the phenol OH with the carbonyl groups of *N*-acetyl fragment attached to 1,2,4-triazin-5-one at the O...O distance of 2.77 Å.

Compound **12** is the first example of complex formation with participation of the  $\sigma^H$ -adduct, as the key intermediate of the  $S_N^H$ -reaction. It is worth mentioning, that upon complex formation ligand **11** does not change its architecture. Due to the presence in ligand **11**, the asymmetric center, the formation of two stereoisomers is possible, and, indeed, both isomers are available in crystal structure of complex **12**. As a result of crystallization they form, successively alternating, the coordinated polymer chain.

Copper (II) complexes of 3-(pyridin-2'-yl)-1,2,4-triazin-5(2*H*)-one derivatives have not so far been described; only the data on copper (II) complexes of 1,2,4-triazine derivatives with aromatic  $\pi$ -electron system similar to  $\alpha,\alpha'$ -bipyridinyl are available in the literature. Main parameters for such complexes are presented in Table V. Comparison of bond lengths



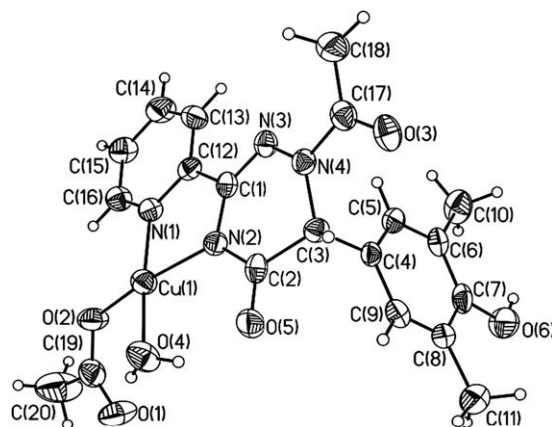
**Scheme 9** Synthesis of the first model compound and its copper (II) complex.



**Figure 1** Molecular structure of 1-acetyl-3-(pyridin-2'-yl)-6-(3',5'-dimethyl-4'-hydroxyphenyl)-1,2,4-triazin-5(2*H*)-one.

shows that increase in electron-donation character of the 1,2,4-triazine ring leads to reinforcement of the Cu—N<sub>Tr</sub> bond. Taking into account practically unchanged chelating angle, as a consequence, the Cu—N<sub>Py</sub> bond length is extended. In case of complex **12** the 1,2,4-triazine ring is not aromatic, therefore, an enhanced electron-donating ability of nitrogen atoms results in a considerable decrease in the Cu—N<sub>Tr</sub> bond length, thus making the complex to be a more stable than the previous ones. Increase in value of the chelating bond angle, and decrease in Cu—N<sub>Py</sub> bond are also features, indicating at a more stable complex formation.

Based on the data obtained for model compounds one can assume that in the process of sorption the attached ligand fragments of polymer **6** exhibit coordination properties like  $\alpha,\alpha'$ -bipyridinyl, while phenol hydroxy groups are not involved in the complex formation. The latter proceeds with incorporation of water and the acetate ion to form polynuclear structures (Fig. 3). As any phenol is a stronger acid than water, the presence of the latter in coordination sphere can be explained by the hindering effect of a bulky phenol substituent. Studying on model compounds structure has revealed that the most



**Figure 2** Molecular structure of copper (II) complex **12**.

TABLE IV  
Selected Bond Lengths (Å) and Bond Angles (deg) for 11 and 12

Structure 11					
N(1)–N(2)	1.395(2)	C(3)–C(7)	1.483(3)	C(15)C(6)C(5)	110.06(18)
C(3)–N(2)	1.280(3)	C(15)–C(6)	1.508(3)	N(1)C(6)C(5)	110.98(18)
C(3)–N(4)	1.383(3)	C(5)–O(1)	1.212(2)	N(1)C(6)C(15)	113.78(18)
C(5)–N(4)	1.355(3)	C–C <sub>benzene ring</sub>	1.381(2)–1.400(2)	N(2)C(3) N(4)	124.83(19)
C(5)–C(6)	1.512(3)	C–C <sub>pyridine ring</sub>	1.368(2)–1.385(2)	C(16)C(15)C(14)	117.6(2)
N(1)–C(6)	1.472(2)	C(12)–O(3)	1.374(3)	C(16)O(3)H(3)	113.67
Structure 12					
Cu(1)–O(4)	1.9504(17)	C(7)–C(6)	1.390(4)	O(2)Cu(1)O(1)	102.34(8)
Cu(1)–O(1)	2.286(2)	C(7)–C(8)	1.384(4)	O(4)Cu(1)O(2)	92.39(8)
Cu(1)–O(2)	1.9566(17)	N(1)–C(16)	1.335(3)	O(4)Cu(1)N(1)	175.39(9)
Cu(1)–N(1)	1.984(2)	N(1)–C(12)	1.345(3)	N(1)Cu(1)N(2)	81.83(9)
Cu(1)–N(2)	1.979(2)	N(2)–C(1)	1.383(3)	O(1)Cu(1)N(1)	88.66(9)

plausible coordination way is the formation of the bridge type dinuclear complexes that require chelating cross-linking of polymer chains. Since cross-links existing in polymers do not allow a macromolecule to accept a conformation, appropriate for chelating, only 8–20% of the theoretical coordination capacity can be realized in practice.

In order to obtain a polymer sorbent, based on phenol-formaldehyde resin, with the highest capacity the targeted synthesis of optimal structure providing participation of phenol hydroxides in complex formation to coordinate with two copper (II) ions has been suggested (Scheme 10). For this purpose, the  $S_N^H$ -reaction has to be carried out under oxidizing conditions to cause aromatization of the 1,2,4-triazine ring. The structure proposed has to ensure a coplanar arrangement of both chelating rings and possibly a high exchange capacity. Therefore, 3-(pyridin-2'-yl)-6-(3',5'-dimethyl-4'-hydroxyphenyl)-1,2,4-triazin-5(2H)-one (13) and its copper (II) complex (14) have been obtained (Scheme 11). Unfortunately, the quality of crystals of 14 made it possible to characterize only coordination environment of the metal.

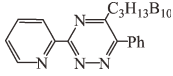
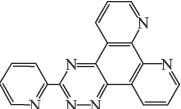
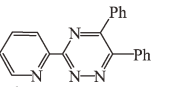
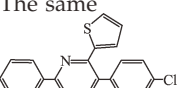
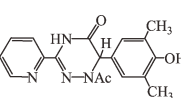
Structure of complex 14 is formed from one molecule of the heterocyclic ligand, the acetate ions, and one molecule of the water. In this complex, there is

only one chelate ring, formed by nitrogen atoms of the pyridine and triazine rings, and, contrary to the expectations, the phenol hydroxide does not take part in complex formation. The obtained complex 14 is the first example of coordination compound, obtained by nucleophilic substitution of hydrogen in the aromatic system of 1,2,4-triazine-5(2H)-one. Comparison of complexes 12 and 14 shows that coordination environment of metal centers is nearly the same, with the difference that donating nitrogen of the triazine ring in the  $\sigma^H$ -adduct 12 is N4, while in substitution product 14—N2.

## CONCLUSION

Use of the  $S_N^H$  methodology enabled us to realize new polymer-analogous transformations of phenol-formaldehyde and resorcinol-formaldehyde resins. It has been demonstrated that for getting sorbents

TABLE V  
Main Bond Lengths (Å) and Bond Angles (deg) for Copper (II) Complexes of 1,2,4-Triazine Derivatives

Formula of ligand	Cu–N <sub>Py</sub> (pyridine)	Cu–N <sub>Tr</sub> (triazine)	N <sub>Py</sub> –Cu–N <sub>Tr</sub>	Ref.
	2.054	2.028	78.74	[15]
	2.011	2.043	80.01	[16]
	2.037	2.033	79.65	[17]
The same	2.032	2.035	80.12	[18]
The same	2.068	2.009	79.28	[19]
	2.014	2.028	79.39	[20]
	1.986	1.981	81.71	Present work

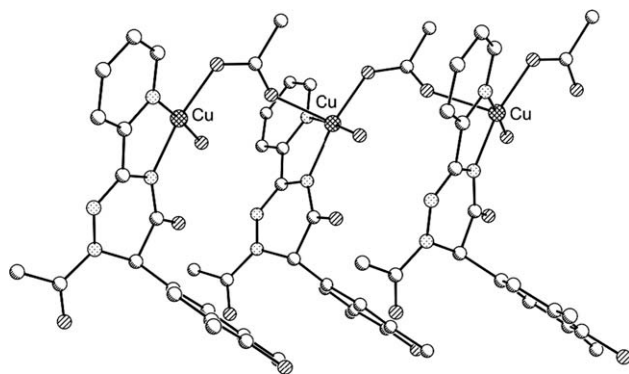
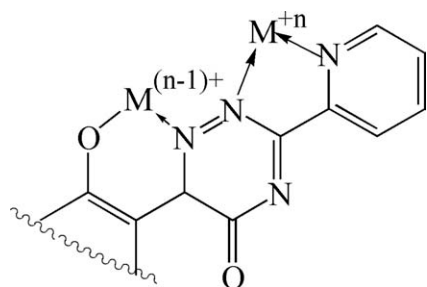
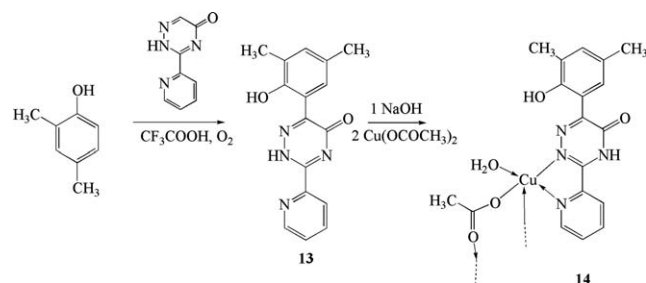


Figure 3 Structure of the chain in copper (II) complex 12.





**Scheme 10** Plausible structure of the complex with participation of the phenol hydroxide.



**Scheme 11** Synthesis of the second model compound and its copper (II) complex.

with a high degree of attached heterocyclic units, phenol-formaldehyde and resorcinol-formaldehyde resins have to be modified with derivatives of 3-(pyridin-2'-yl)-1,2,4-triazin-5(2H)-ones, as one of the most reactive electron-deficient species, and also as compounds capable of complexing with metals. All sorbents obtained have exhibited selectivity toward copper (II) ions. Sorbents with a higher sorption capacity can be obtained through the template synthesis. Studying on the structure of model compounds shows that the most plausible way of copper (II) coordination is formation of the bridge type dinuclear complexes that require chelating cross-linking of the polymer chains.

## References

- Sahni, S. K.; Reedijk, J. *Coord Chem Rev* 1984, 59, 1.
- Varma, A. J.; Deshpande, S. V.; Kennedy, J. F. *Carbohydr Polym* 2004, 55, 77.
- Chupakhin, O. N.; Charusnin, V. N.; van der Plas, H. C. *Nucleophilic Aromatic Substitution of Hydrogen*; Academic Press: N.Y., San Diego, 1994.
- Makosza, M.; Wojciechowski, K. *Chem Rev* 2004, 104, 2631.
- Charushin, V. N.; Chupakhin, O. N. *Mendeleev Commun* 2007, 17, 249.
- Chupakhin, O. N.; Rusinov, G. L.; Beresnev, D. G.; Itsikson, N. A. *Russ J Org Chem* 1999, 35, 1253.
- Beresnev, D. G.; Itsikson, N. A.; Chupakhin, O. N.; Charushin, V. N.; Kodess, M. I.; Butakov, A. I.; Rusinov, G. L.; Morzherin, Y. Y.; Kononov, A. I.; Antipin, I. S. *J Org Chem* 2006, 71, 8272.
- Chupakhin, O. N.; Rusinov, G. L.; Itsikson, N. A.; Beresnev, D. G.; Nikolaeva, I. L.; Burirov, A. R.; Kononov, A. I. *Heterocycl Commun* 2004, 10, 14.
- Chupakhin, O. N.; Pestov, A. V.; Yatluk, Y. G. *Russ Chem Bull* 2009, 57, 256.
- Sorenson, W. R.; Campbell, T. W. *Preparative Methods of Polymer Chemistry*; Intersci. Publ: London, 1961.
- Chupakhin, O. N.; Rusinov, G. L.; Beresnev, D. G.; Neunhoeffer, H. *J Heterocyclic Chem* 1997, 34, 573.
- Sheldrick, G. M. SHELX-97 Release 97-2; University of Goettingen: Germany, 1998.
- Kozhevnikov, D. N.; Ulomsky, E. N.; Rusinov, V. L.; Chupakhin, O. N.; Neunhoeffer, H. *Mendeleev Commun* 1997, 7, 116.
- Rusinov, V. L.; Kozhevnikov, D. N.; Kovalev, I. S.; Chupakhin, O. N.; Aleksandrov, G. G. *Russ J Org Chem* 2000, 36, 1050.
- Prokhorov, A. M.; Kozhevnikov, D. N.; Rusinov, V. L.; Chupakhin, O. N.; Glukhov, I. V.; Antipin, M. Y.; Kazheva, O. N.; Chekhlov, A. N.; Dyachenko, O. A. *Organometallics* 2006, 25, 2972.
- Zou, X.-H.; Cai, J.-W.; Feng, X.-L.; Hu, X.-P.; Yang, G.; Zhang, H.; Ji, L.-N. *Transition Met Chem* 2001, 26, 704.
- Uma, R.; Palaniandavar, M.; Butcher, R. J. *J Chem Soc Dalton Trans* 1996, 2061.
- Teoh, S. G.; Eltayeb, N. E.; Fun, H.-K.; Ibrahim, K.; Rosli, M. M. *Acta Crystallogr Sect E* 2007, 63, m1182.
- Soudi, A. A.; Marandi, F.; Morsali, A.; Kempe, R.; Hertle, I. *J Coord Chem* 2005, 58, 1631.
- Kozhevnikov, D. N.; Kozhevnikov, V. N.; Prokhorov, A. M.; Ustinova, M. M.; Rusinov, V. L.; Chupakhin, O. N.; Aleksandrov, G. G.; König, B. *Tetrahedron Lett* 2006, 47, 869.