Journal of
the Serbian
Chemical Society

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J. Serb. Chem. Soc. *84* (12) 1391–1404 (2019)
JSCS–5272

UDC 541.572.54+546.562–71:539.217+
66.081:678–13
Original scientific paper

Design of an amino-functionalized chelating macroporous copolymer poly(GMA-*co*-EGDMA) for the sorption of Cu(II) ions

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(Received 21 January, revised 12 April, accepted 15 April 2019)

Abstract: Polymer-based, highly porous nanocomposites with functionalized ligands attached to the core structure are extremely efficient in the detection, removal and recovery of metals through the process of sorption. Quantum-chemical models could be helpful for sorption process analyses. The sorption of Cu(II) ions by amino-functionalized chelating macroporous copolymers poly(GMA-*co*-EGDMA)-amine and sorption selectivity of the subject copolymers, ethylenediamine (en), diethylenetriamine (dien) and triethylenetetramine (trien), were successfully modelled by quantum chemical calculations. Considering the crystal structures from CSD and experimental conditions during the formation of metal complexes, the most frequent mononuclear complexes are those with the tetradentate teta ligand, while binuclear complexes are formed when the metal ion is in large excess. Although the en-copolymer was the most effective functionalized one, higher maximum sorption capacities ($Q_{\max}$) were observed for the dien- and trien-copolymers, due to their abilities to form binuclear complexes. The enthalpy term has the greatest contribution to the total Gibbs energy change of reaction for the formation of mononuclear Cu(II) complexes (ΔG_{aq}), while the solvation energy of the reaction has the greatest contribution in the formation of binuclear complexes. The results of the study indicate that small amines with the ability to form binuclear complex are the best choice for functionalization of the considered copolymer.

Keywords: sorption of metal ions; amino-functionalized copolymer; DFT modelling; coordination isomers; CSD.

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https://doi.org/10.2298/JSC190125031S

INTRODUCTION

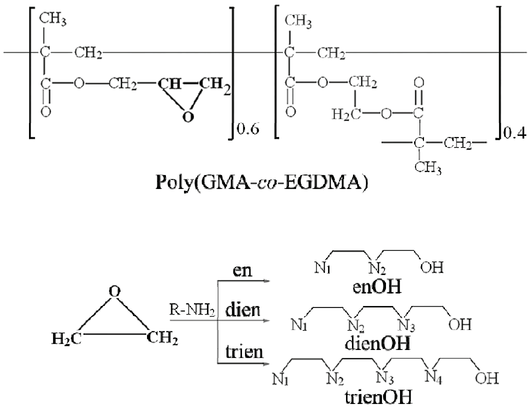
The Earth's crust naturally contains heavy metal compounds, the concentration of which is increased in places such as bedrocks, or can be found as ores in rocks. Unfortunately, heavy metals are constantly being released into the environment from anthropogenic sources: metalliferous mining and smelting (As, Cd, Pb, Hg), industry (As, Cd, Cr, Co, Cu, Hg, Ni, Zn), atmospheric deposition (As, Cd, Cr, Cu, Pb, Hg, U), agriculture (As, Cd, Cu, Pb, Si, U, Zn) and waste disposal (As, Cd, Cr, Cu, Pb, Hg, Zn).[1–3] Consequently, the amounts of heavy metals deposited on the Earth's surface are considerably higher compared to natural background concentrations. Heavy metals accumulate over time and since they are non-decomposable or non-biodegradable, they are the long-term health and environmental hazards. Very rarely, acute effects appear when considerable amounts of heavy metals are accidentally released into the environment.[4] Various methods of heavy metal removal have been developed and are still being developed: physicochemical (membrane filtration, chemical precipitation, ion-exchange, adsorption), electrochemical (electrocoagulation, electroflotation, electrodeposition) biological[5] (biosorption, by bacteria and microorganism, activated sludge process, biofilter, anaerobic digestion, stabilization ponds) and current (membrane filtration, photo-catalysis, nanotechnology) methods. Process of sorption is efficient in the detection and removal of heavy metals.[6] Recently, nanocomposite carbon-[7] (activated carbon, carbon nanotubes, fullerenes, graphene), polymer-[8,9] silica-[10–20] and natural-based[21–24] nanocomposites, highly porous materials designed for heavy metal adsorption, are being intensively developed.[6] The features of the above-mentioned composites are environmental stability, high specific surface area and strength of the core (carbon, polymer and silica), and in synergy with the reactivity of attached ligands to specific metal ions make them efficient, specific and sensitive metal ions sorbents. This allows fast and cheap detection, complete removal or recovery of metals from contaminated waters.

Although essential, Cu oligoelement is important, above all, for the activity of enzymes in living organisms,[25,26] it becomes very toxic[27] when present in excessive levels. This metal is classified as highly hazardous to human health and the environment with various long-term detrimental effects. There is a great interest in Cu(II) remediation in terms of phase transfer or its transformation into harmless chemical forms. In order to protect the quality of soil and water pollution, many countries instituted rigorous environmental regulations.[28] Mesoporous silica with attached 3-{[3-(methoxycarbonyl)benzylidene]hydrazinyl}-benzoic acid,[29] 3-{[(4-ethoxy-2-mercaptophenyl)imino]methyl}salicylic acid,[30] 3-{[2-(2-hydroxy-1-naphthoyl)hydrazono]methyl}benzoic acid,[31] 4-*tert*-butyl-2--hydroxybenzaldehyde thiosemicarbazone,[32] 3-[[[4-[[(3-carboxyphenyl)methylene]amino]-2,5-dihydro-5-oxo-1*H*-pyrayol-3-yl]imino]methyl]benzoic acid,[33] 2,2'-[(4,5-dimethyl-1,2-phenylene)bis(nitrilomethylidene)bis[phenol],[34] 2,2’-[(1,2-ethanediylbis(thio-2,1-phenylenenitrilomethylidene)]bis[phenol],[35] 2,3-dihydro-5,6-bis[[(2-hydroxyphenyl)methylene]amino]-2-thioxo-4(1*H*)-pyrimidinone,[36] *E*,*E*,*E*,*E*-3,3′,3″,3‴-[2,3,6,7-naphthalenetetrayltetrakis(nitrilomethylidyne)tetrakis[2-hydroxybenzoic acid],[37] 2,2’-(1,8-octanediylidenedinitrilo)-bis[4,6-dimethylphenol][38] are used as optical nanosensors for selective adsorption, detection and removal of Cu(II) ions.[36] The mentioned materials are very sensitive, changing their colour when Cu(II) ions are present even in traces. Any additional procedure or equipment besides the silica complexes is not necessary for the detection of Cu(II) ions.

The physicochemical method of remediation through precipitation of Cu(II) ions using chelating agents has proved to be very efficient in fulfilling environmental regulation guidelines.[39] Chelating homopolymers and copolymers are highly selective sorbents of heavy metal ions from aqueous solutions.[40] Efficient and selective polymers consist of cross-linked polymer structures (core) and functional groups (ligands) that have the ability to form adequate interactions with heavy metals. These functional groups are the key for the selective chelation of heavy metals. Within functional groups, coordination bonding with metal ions is achieved through N, O, P and S atoms.[41,42]

Macroporous copolymers based on glycidyl methacrylate (GMA) are especially interesting, since they contain an epoxide ring in their structures. Optionally, the ease of opening the epoxide ring offers the possibility for the introduction of a ligand with an iminodiacetate, thiol, pyrazole or amino group.[43] The GMA molecule is a convenient basis for the relatively simple formation of different metal ions and organic compound sorbents. Therefore, the structure of a GMA-based copolymer suggests promising possibilities of numerous applications referring to environmental issues.[41,42,44–49]

An incredible number of possible structures that could be synthesized, demands a theoretical evaluation of the most appropriate ligand for the sorption of a particular compound. Recently, through the process of polymerization of GMA monomer together with ethylene glycol dimethacrylate (EGDMA), a macroporous copolymer poly(glycidyl methacrylate-*co*-ethylene glycol dimethacrylate) (poly(GMA-*co*-EGDMA)) has been synthesised. The final products were obtained through functionalization of the copolymer poly(GMA-*co*-EGDMA) with three different amines (Scheme 1): ethylenediamine in poly(GMA-*co*-EGDMA)-en, diethylenetriamine in poly(GMA-*co*-EGDMA)-dien and triethylenetetramine in poly(GMA-*co*-EGDMA)-trien. These three amino-functionalized copolymer samples showed differences in the efficacy of Cu(II) sorption from aqueous solutions, which is expressed as the polymer capacity of sorption in mmol of adsorbed ions per gram of the polymer, Q (mmol g^{-1}). The process of sorption itself is a rapid one, while the capacity of sorption depends on the ligand. The sorption capacity rises from -en to -dien (around 1.75 times larger), but there is no difference for -dien and -trien copolymer, *i.e.*, the values are practically identical.[40]



Scheme 1. The structure of chelated copolymer poly(GMA-*co*--EGDMA), functionalized through the reaction of amines (en, dien and trien) with the epoxide ring of the original copolymer.

The aim of this study was to explain experimentally the obtained trend for Cu(II) by applying theoretical techniques to predict the selectivity of the ligands. The complex molecular system of each of the three copolymers is comprised of a recurring structural unit. Therefore, it is possible to discuss Cu(II) ion and copolymer reactions within the macromolecule at the unit segment level. The unit segment would be the Cu(II) ion with coordinated amino ligands. A large number of such segments (up to several thousands) that can be found in the solution where the sorption occurs include a sorbent/metal ion system. The unit segment, crucial for metal–ligand bonding is, in itself, a complex of metal ions and amino ligands, the geometry and stability of which can be predicted by statistical analysis of data taken from the crystal structures and quantum chemical calculations.

METHODOLOGY

Possible coordination modes of triethylenetetramine (trien) ligand in crystal structures, extracted from Cambridge Structural Database (CSD, version 5.38, November 2016),[51] were investigated by applying statistical analysis of the obtained data.

The quantum chemical calculations were performed in the Gaussian09 program[52] applying the B3LYP functional. The 6-311++g** basis set was used for non-metal elements and the lanl2dz basis set for Cu^{2+}. The initial complex geometries of possible isomers were optimized at the same level of theory, and the parameters obtained by optimization were used to evaluate Gibbs free energies for the reactions of complex formation. In these reactions (Eq. (1)), the hydroxyamine obtained in the ring opening reaction (marked as L), reacts with the hexaaqua complex, forming the corresponding complex with the coordinated amine:

$$a[\mathrm{Cu(H_2O)_6}]^{2+} + \mathrm{L} \rightarrow [\mathrm{Cu_a(H_2O)}_{6a-n}(\mathrm{L})]^{2+} + n\mathrm{H_2O} \qquad (1)$$

In Eq. (1), L represents enOH, dienOH or trienOH ligand (Scheme 1), n represents the hapticity of ligands, while a equals 1 for mononuclear and 2 for binuclear complexes. The

SMD method and the aforementioned level of theory were applied for the solvation energy (ΔE_s) calculations (Eq. (2)):

$$\Delta E_{\mathrm{s(r)}} = \sum E_{\mathrm{s(product)}} - \sum E_{\mathrm{s(reactants)}} \tag{2}$$

The Gibbs energy change of reaction (1) in aqueous solution (ΔG_aq) was estimated according to the following equation:

$$\Delta G_\mathrm{aq} = \Delta G_\mathrm{g} + \Delta E_{\mathrm{s(r)}} \tag{3}$$

ΔG_g, the Gibbs energy change of the reaction (1) in vacuum (Eq. (4)), includes the enthalpy change (ΔH) and entropy change (ΔS), connected through the following equation:

$$\Delta G_\mathrm{g} = \Delta H - T\Delta S \tag{4}$$

The enthalpy change of the reaction is determined by Eq. (5):

$$\Delta H = \Delta E_\mathrm{e} + \Delta E_\mathrm{t} + p\Delta V \tag{5}$$

in which ΔE_e stands for the electronic energy change, ΔE_t is the thermal energy change, and $p\Delta V$ is the work performed in a reaction.

RESULTS AND DISCUSSION

Crystallographic analysis of the structures from CSD

Crystal structure analysis is a very useful tool used in conformational analysis and in supramolecular chemistry. In this particular case, the primary interest was to gather information from the crystal structure analysis about coordination geometries of complexes with Cu(II) ion and the trien ligand, as well as the abundance of each geometry observed. Considering the complexes of Cu(II) and the substituted trien ligand from CSD, the most frequent ones are mononuclear complexes of the Cu(II) ion with tetradentate trien ligand geometries, while the second most abundant are binuclear complexes in which two N atoms of the trien ligand are coordinated to each metal ion. Taking into consideration the experimental conditions during trien complex formation, it was observed that binuclear binding occurs when the metal ion is in excess compared to the trien ligand (more than two times). The abundance of mononuclear complexes of Cu(II) and the tetradentate trien ligand are distributed as follows: by far the most frequent are those with square pyramidal (71 %), followed by octahedral (26 %) and square planar (3 %) complex geometry.

When only the Cu(II) complexes with unsubstituted trien ligand (17 crystal structures) are taken into account, a similar trend was observed. Mononuclear complexes with the tetradentate trien ligand are the most frequent (10 structures), while binuclear (2 structures) and polynuclear complexes (5 structures) with the tetradentate trien ligand are less abundant (Fig. 1). Structures with a bridging trien ligand were not found. Complexes with a square-pyramidal geometry (15 structures) are much more numerous than complexes with a square-planar geometry (2 structures). The values of the torsion angle T (N1–N2–N3–N4 angle) are in the range from 0 to 20°, indicating a planar or *trans* conformation of the trien ligand.

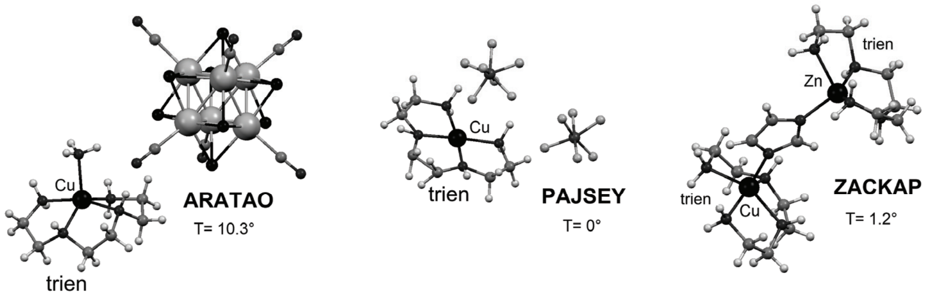


Fig. 1. The fragments of crystal structures with the square-pyramidal Cu(II) complex (refcode ARATAO), the square-planar Cu(II) complex (refcode PAJSEY), and the mixed binuclear complex (with Cu(II) and Zn(II) metal ion) with a tetradentate trien ligand (refcode ZACKAP).

Experimental conditions during the sorption of Cu(II) ions for functionalized copolymers

As previously concluded, the quantity ratio of metal ions and ligands influences the mode in which the ligand is coordinated to the metal. For that purpose, both the quantity of Cu(II) ions and the corresponding copolymer amino-functionalized groups were determined (Table I), in sorption studies of the Cu(II) ion.[42] Poly(GMA-*co*-EGDMA)-en contains 1.12 mmol, poly(GMA-*co*-EGDMA)-dien 0.81 mmol and poly(GMA-*co*-EGDMA)-trien) 0.65 mmol amino-functionalized groups.[42] Considering the number of amino-functionalized groups (*fg*) in the copolymer, the quantity of the metal ion is significantly higher in all three cases (Table I). The Cu(II) ion is in an excess, so the complete quantity of the Cu(II) ion would not be sorbed. If the Cu(II) ions formed the mononuclear enOH, dienOH or trienOH complexes, the maximum sorption ($Q_{\max} = f(t)$) would be different. According to the number of amino-functionalized groups, en-functionalized copolymer should have the highest and the trien-functionalized one should have the lowest $Q_{\max}$ value. However, dien- and trien-functionalized copolymers have greater $Q_{\max}$ values. One of the reasons could be the ability of these ligands to form binuclear complexes. The en-functionalized copolymer is the most effectively functionalized one (53 %), followed by the dien- (38 %) and trien-functionalized copolymer (31 %), which is inverse to their molecular lengths. Similar $Q_{\max}$ values of dien- and trien-ligands are quite unlikely given the number of functionalized groups. However, the shortest amine (en) more easily penetrates inside the initial poly(GMA-*co*-EGDMA) copolymer, thus functionalizing a larger number of epoxide rings.

In aqueous solutions Cu(II) ion exists as a hexaaqua complex. The sorption of this metal strongly depends on the ability of its hexaaqua complex to penetrate near the amino-functionalized groups of the corresponding copolymer. This complex is more voluminous and less flexible than the considered amines (en, dien and trien), resulting in its lower penetrability than the amines. Indicators are the theoretical Q_{max} values (Table I), which are in cases of en-functionalized and dien-functionalized copolymers significantly higher than the experimentally determined Q_{max} values.

TABLE I. The quantities of Cu(II) ions and amino-functionalized groups (in mmol) in the corresponding copolymer, obtained in the process of the experimentally conducted sorption of Cu(II) ions. Theoretically $Q_{max(theor)}$ and experimentally $Q_{max(exp)}$ determined values of the maximum sorption of Cu(II) ion, expressed in mmol g^{-1}

Copolymer	$n(Cu^{2+})$	n(fg)[a]	$Q_{max(theor)}$[b] mononuclear	$Q_{max(theor)}$[c] binuclear	Q_{max} (exp)
poly(GMA-*co*-EGDMA)-en	2.5	2.24	2.24	4.48	1.40
poly(GMA-*co*-EGDMA)-dien	2.5	1.62	1.62	3.24	2.45
poly(GMA-*co*-EGDMA)-trien	2.5	1.30	1.30	2.60	2.40

[a]The quantities of functionalized groups (fg) are calculated per g of the copolymer sample used in the experiments; [b]theoretical Q_{max} values calculated per g of the copolymer, considering that mononuclear Cu(II) complexes are formed; [c]the theoretical Q_{max} values calculated per g of the copolymer, considering that binuclear Cu(II) complexes are formed

Quantum chemical calculations for trienOH complexes

To confirm the above-proposed assumption, quantum chemical calculations were performed to evaluate the Gibbs energy change (ΔG_{aq}) that accompanies the formation of mononuclear and binuclear Cu(II) complexes with the trienOH ligand in aqueous solution. For this purpose, the complex geometries obtained through optimization of four possible isomers of mononuclear complexes and one binuclear Cu(II) complex were used. Depending on the mutual positions of coordinated oxygen atoms from aqua and trienOH ligands, initial isomers of octahedral complexes with pentadentate trienOH ligand (N_1,N_2,N_3,N_4,O-trienOH) could be a *cis* or *trans* isomer. Upon the optimization, dissociation of a water molecule (Wd) from an octahedral mononuclear complex occurs. The newly formed complexes take square pyramidal geometry (Fig. 2).

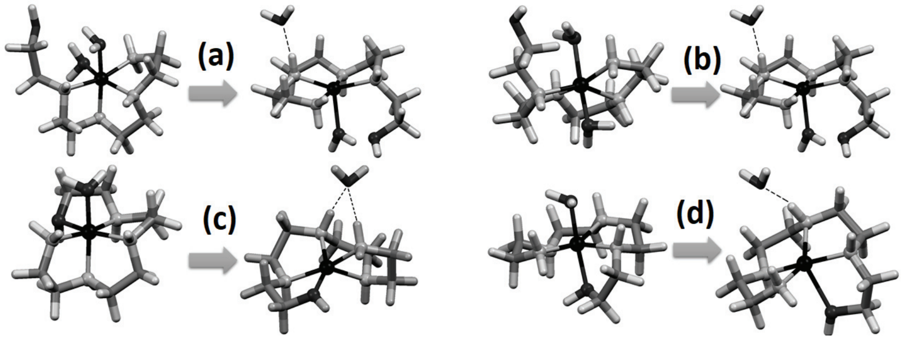


Fig. 2. Optimization of possible isomers of mononuclear Cu(II) complexes with the trienOH ligand.

The apical position is occupied by an OH group ([Cu(N_1,N_2,N_3,N_4,O-trienOH)]$^{2+}$ complex), or by the NH group of the trienOH ligand ([Cu(N_1,N_3,N_4,O,N_2-trienOH)]$^{2+}$ complex):

a) *cis*-[Cu(H_2O)$_2$(N_1,N_2,N_3,N_4-trienOH)]$^{2+}$ →
   [Cu(H_2O)(N_1,N_2,N_3,N_4-trienOH)]$^{2+}$ + H_2O
b) *trans*-[Cu(H_2O)$_2$(N_1,N_2,N_3,N_4-trienOH)]$^{2+}$ →
   [Cu(H_2O)(N_1,N_2,N_3,N_4-trienOH)]$^{2+}$ + H_2O
c) *cis*-[Cu(H_2O)(N_1,N_2,N_3,N_4,O-trienOH)]$^{2+}$ →
   [Cu(N_1,N_3,N_4,O,N_2-trienOH)]$^{2+}$ + H_2O
d) *trans*-[Cu(H_2O)(N_1,N_2,N_3,N_4,O-trienOH)]$^{2+}$ →
   [Cu(N_1, N_2,N_3,N_4,O-trienOH)]$^{2+}$ + H_2O

The tetradentate N_1,N_2,N_3,N_4-trienOH ligand in octahedral mononuclear complexes leaves a space for two aqua ligands in the *cis* or *trans* positions. Optimized complexes take square pyramidal geometry, likewise in complexes with pentadentate trienOH ligand (Fig. 2). One of the aqua ligands is released, while the other one remains in the apical position of the square pyramidal ([Cu(H_2O)(N_1,N_2,N_3,N_4-trienOH)]$^{2+}$) complex. As far as the coordinated N atoms are concerned, they are in equatorial position (*trans* geometry of a tetradentate ligand).

The structures obtained by the optimization were used to calculate the Gibbs free energy change in the formation reaction of these complexes out of the Cu(II) hexaaqua complex (Eq. (1)).

Interestingly, the results of the optimization are in agreement with the results of the crystallographic analysis, which is strong confirmation that the square pyramidal geometry of the Cu(II) complexes is the most frequent one in crystal structures.

The enthalpy of the formation reaction of Cu(II) complexes with the trienOH ligand, corresponding to the sum of electronic energy change (ΔE_e), thermal energy change (ΔE_t), and work ($p\Delta V$), has the greatest contribution to the total Gibbs energy change in aqueous solution (ΔG_{aq}).

An exothermal process is indicated by the negative sign of enthalpy. On the other hand, contributions from the entropy ($T\Delta S$ term) and solvation energy ($\Delta G_{aq}-\Delta G_g$) are significantly lower than those from the enthalpy term. The formation of a complex without coordinated OH-group is energetically more favourable, by only about 5 % (Table II).

The structure the geometry of which is based on crystallographic data was used as a model system for quantum chemical calculations for binuclear Cu(II) complexes with the trienOH ligand. The first two N atoms (N_1 and N_2) are coordinated to one Cu(II) ion in the square pyramidal complex, while the other two N atoms (N_3 and N_4) along with the OH group are coordinated to the second Cu(II) ion (Fig. 3). Upon the optimization, one aqua ligand was dissociated from the Cu(II) ion to which the N_1 and N_2 atoms of the trienOH ligand are coordinated, leading to a change towards the square planar geometry of that Cu(II) ion. The other Cu(II) ion remains in the square pyramidal geometry. The enthalpy change of this reaction has positive sign (endothermal reaction), which is compensated by the entropic term ($T\Delta S$). However, the greatest contribution to the spontaneous nature of the reaction originates from the solvation energy of the reaction.

TABLE II. The calculated results of the thermodynamic functions (kcal* mol^{-1}) for the thermo-chemical analysis in the process of the formation of Cu(II) complexes with the trienOH ligand

Optimized metal complex	ΔE_e	ΔE_t	$p\Delta V$	$T\Delta S$	ΔG_g	ΔG_{aq}
Mononuclear trienOH complexes						
trans-[Cu(H$_2$O)(N_1,N_2,N$_3$,N_4-trienOH)]$^{2+}$	–411.5	21.3	–1.2	23.3	–414.7	–410.9
trans-[Cu(H$_2$O)(N_1,N_2,N_3,N_4-trienOH)]$^{2+}$	–411.5	21.3	–1.2	23.3	–414.7	–410.9
[Cu(N_1,N_3,N_4,O,N_2-trienOH)]$^{2+}$	–389.9	4.1	–0.6	13.4	–399.8	–395.9
[Cu(N_1,N_2,N_3,N_4,O-trienOH)]$^{2+}$	–396.4	4.1	–0.6	13.2	–406.2	–402.2
Binuclear trienOH complex						
[Cu(H$_2$O)$_2$(N_1,N_2:N_3,N_4,O-trienOH)(H$_2$O)$_2$Cu]$^{4+}$	135.4	–8.8	3.0	130.5	–1.0	–344.8

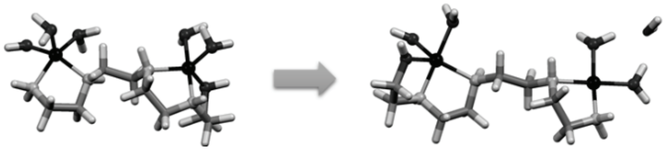


Fig. 3. The optimization of the binuclear Cu(II) complex with the trienOH ligand.
[Cu(H$_2$O)$_3$(N_1,N_2:N_3,N_4,O-trienOH)(H$_2$O)$_2$Cu]$^{4+}$ →
[Cu(H$_2$O)$_2$(N_1,N_2:N_3,N_4,O-trienOH)(H$_2$O)$_2$Cu]$^{4+}$ + H$_2$O

Quantum chemical calculations for enOH and dienOH complexes

As in the trienOH complexes, the initial structures of all possible isomers of mononuclear enOH and dienOH complexes of Cu(II) ion were optimized, with the geometries of all possible coordination isomers (Table III). The optimized structures of the complexes with the highest values of the Gibbs energy changes for reactions of the complex formation in an aqueous solution (ΔG_{aq}) are shown in Fig. 4.

Unlike the most stable dienOH complex, the most stable structure of an enOH complex does not contain a coordinated OH group. Both enOH and dienOH complexes have higher ΔG_{aq} values than those of trienOH complexes, while dienOH complex displayed the highest ΔG_{aq} value. This trend could be

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* 1 kcal = 4184 J

explained by a larger number of chelate rings in the dienOH complex, compared to the enOH complex. Although the most stable trienOH complex has the greatest number of chelate rings, it is the least stable complex, since chelate rings are condensate and, as such, under a higher ring strain than the rings of the most stable dienOH complex.

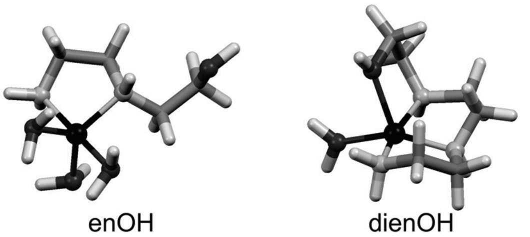

Fig. 4. Optimized Cu(II) complexes with the enOH ($[\mathrm{Cu(H_2O)_3}(N_1,N_2\text{-enOH})]^{2+}$) and dienOH (*trans*-$[\mathrm{Cu(H_2O)}(N_1,N_2,N_3,O\text{-dienOH})]^{2+}$) ligands having the highest values of the Gibbs energy change (ΔG_{aq}) for the reaction of metal complex formation in aqueous solutions.

TABLE III. The calculated results of the thermodynamic functions (kcal mol^{-1}) for the thermochemical analysis in the process of formation the mononuclear Cu(II) complexes with enOH or dienOH ligand

Optimization of the metal complexes	ΔE_e	ΔE_t	$p\Delta V$	$T\Delta S$	ΔG_g	ΔG_{aq}
Mononuclear enOH complexes						
$mer\text{-}[\mathrm{Cu(H_2O)_3}(N_1,N_2,O\text{-enOH})]^{2+}\rightarrow mer\text{-}[\mathrm{Cu(H_2O)_2}(N_1,N_2,O\text{-en}OH)]^{2+}+\mathrm{H_2O}$	–372.8	36.8	–0.6	–29.0	–365.6	–361.7
$fac\text{-}[\mathrm{Cu(H_2O)_3}(N_1,N_2,ii\text{-enOH})]^{2+}\rightarrow mer\text{-}[\mathrm{Cu(H_2O)_2}(N_1,N_2,O\text{-enOH})]^{2+}+\mathrm{H_2O}$	–372.8	36.8	–0.6	–29.0	–365.6	–361.7
$[\mathrm{Cu(H_2O)_4}(N_1,N_2\text{-enOH})]^{2+}\rightarrow [\mathrm{Cu(H_2O)_4}(N_1,N_2\text{-enOH})]^{2+}$	–404.3	71.2	0	–48.1	–381.2	–375.4
$[\mathrm{Cu(H_2O)_3}(N_1,N_2\text{-enOH})]^{2+}\rightarrow [\mathrm{Cu(H_2O)_3}(N_1,N_2\text{-enOH})]^{2+}$	–388.6	9.3	0	–39.4	–418.6	–414.8
Mononuclear dienOH complexes						
$trans\text{-}[\mathrm{Cu(H_2O)_2}(N_1,N_2,N_3,O\text{-dienOH})]^{2+}\rightarrow trans\text{-}[\mathrm{Cu(H_2O)}(N_1,N_2,N_3,O\text{-dienOH})]^{2+}+\mathrm{H_2O}$	–388.3	20.6	–0.6	63.4	–431.6	–429.0
$cis\text{-}\alpha\text{-}[\mathrm{Cu(H_2O)_2}(N_1,N_2,N_3,O\text{-dienOH})]^{2+}\rightarrow cis\text{-}\beta\text{-}[\mathrm{Cu(H_2O)}(N_1,N_2,N_3,O\text{-dienOH})]^{2+}+\mathrm{H_2O}$	–385.1	20.6	–0.6	35.8	–400.9	–398.1
$cis\text{-}\beta\text{-}[\mathrm{Cu(H_2O)_2}(N_1,N_2,N_3,O\text{-dienOH})]^{2+}\rightarrow cis\text{-}\beta\text{-}[\mathrm{Cu(H_2O)}(N_1,N_2,N_3,O\text{-dienOH})]^{2+}+\mathrm{H_2O}$	–385.1	20.6	–0.6	35.8	–400.9	–398.1
$mer\text{-}[\mathrm{Cu(H_2O)_3}(N_1,N_2,N_3\text{-dienOH})]^{2+}\rightarrow [\mathrm{Cu(H_2O)}(N_1,N_2,N_3\text{-dienOH})]^{2+}+2\mathrm{H_2O}$	–364.2	20.2	–1.2	20.4	–365.5	–362.9
$fac\text{-}[\mathrm{Cu(H_2O)_3}(N_1,N_2,N_3\text{-dienOH})]^{2+}\rightarrow [\mathrm{Cu(H_2O)}(N_1,N_2,N_3\text{-dienOH})]^{2+}+2\mathrm{H_2O}$	–364.2	20.2	–1.2	20.4	–365.5	–362.9

CONCLUSIONS

By comparing the Gibbs energy change (ΔG_{aq}) for mononuclear and binuclear trienOH complex, it could be concluded that the formation of mononuclear complexes is a slightly more favourable (spontaneous) process. These results are in agreement with the combined potentiometric–spectrophotometric study of a

Cu(trien) complex,[52] which showed that the mononuclear complex with a tetradentate trien ligand is dominant. This type of complex already occurs at pH 2.5, reaching its maximum at pH 5. In that study, a binuclear complex was not experimentally detected, which could be explained by the fact that the synthesis is conducted in a solution in which the quantity of ligands is four times that of Cu(II) ions. However, it is possible to calculate the equilibrium constant of the reaction in the process of complex formation from the Gibbs energy change ($\Delta G = -RT\ln K$). The functional dependence of this equilibrium constant *versus* the $[Cu(H_2O)_6]^{2+}$ complex concentration is linear in the reaction where a mononuclear complex is formed, or square for binuclear complex formation. In accordance with the Le Chatelier principle, an increase in metal ion concentration shifts the equilibrium towards trienOH complex formation. As a surplus in concentration of Cu(II)aqua complex *versus* trienOH ligand is more pronounced, the proportion of binuclear complex in the product increases. Therefore, it is reasonable to assume that, in case of a trien-functionalized complex, the adsorption of Cu(II) ion occurs as a result of the formation of binuclear complexes, since the concentration of Cu(II) ions is about four times higher than the quantity of ligands (functionalized groups of copolymers). For the same reasons, the formation of binuclear complexes with a dien-functionalized copolymer could be expected, but in this case, the concentration of Cu(II) ions is three times that of ligands.

Finally, the results of this study clearly indicate that amines with three nitrogen ligator atoms are preferable (due to the possibility of binuclear complex formation). However, the more ligator atoms it contains, the more difficult it is for the amine to diffuse inside the polymer. On the other hand, a higher number of ligator atoms increases the strain of chelate rings and reduces the stability of amino-functionalized complex with the sorbed ion.

Acknowledgements. This work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Project No. OI 172043, 172023 and III 43009). Numerical simulations were run on the PARADOX supercomputing facility at the Scientific Computing Laboratory of the Institute of Physics Belgrade, supported in part by the Ministry of Education, Science and Technological Development of the Republic of Serbia.

ИЗВОД

ДИЗАЈН АМИНОФУНКЦИОНАЛИЗОВАНИХ ХЕЛАТНИХ МАКРОПОРОЗНИХ КОПОЛИМЕРА поли(ГМА-*ко*-ЕГДМА) ЗА СОРПЦИЈУ Cu(II) ЈОНА

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Квантнохемијско моделовање се показало као корисна алатка за разјашњавање процеса сорпције, као и за предвиђање структуре насталих производа те сорпције. Уз помоћ квантнохемијских прорачуна успешно су моделаовани процеси сорпције Cu(II) јона и селективност тих сорпција на амино-функционализованим хелатним кополимерима поли(глицидил-метакрилат-*ко*-етиленгликол-диметакрилат) (поли(GMA-*ко*-EGDMA)) са различитим бројем амино група у свом саставу (етилен (-en), диетилентриамин (-dien) и триетилентетраамин (-trien) кополимери). Узимајући у обзир кристалне структуре из CSD и експерименталне услове приликом формирања комплекса са Cu(II) јоном, дошли смо до закључака да су најчешће структуре мононуклеарних комплекса са тетрадентатно везаним лигандима, али да се бинуклеарни комплекси јављају када је јон метала у вишку у односу на кополимер. Без обзира на то што је кополимер са en-лигандима најефикасније функционализован, најбоља сорпција Cu(II) јона (Q_{max}) се, ипак одиграва на dien- и trien-кополимерима. Овакав резултат је последица боље способности dien и trien лиганада за грађење бинуклеарних комплекса са Cu(II) јонима. Највећи допринос укупној промени Гибсове енергије реакције грађења мононуклеарног Cu(II) комплекса (ΔG_{aq}) потиче од енталпијског члана. Међутим, пресудну улогу на формирање бинуклеарних комплекса има солватациона енергија. Резултати наше студије показују да су краћи амини са могућношћу формирања бинуклеарних комплекса најбољи избор приликом функционализације разматраних кополимера за потребе сорпције Cu(II) јона.

(Примљено 21. јануара, ревидирано 12. априла, прихваћено 15. априла 2019)

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