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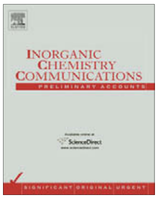

Nanodimensional microreactors encapsulation of 15- and 16-membered diaza dioxa macrocyclic Schiff-base copper(II) complex nanoparticles: Synthesis and characterization

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ABSTRACT

Copper(II) complexes with 15- and 16-membered diaza dioxa Schiff-base macrocyclic ligands "[Cu(R[15 or 16]N_2O_2)]$^{2+}$ (R = Et, Pr, Ph, Ch)" were entrapped in the nanopores of zeolite-Y by a three-step process in the liquid phase: (i) exchange of Cu(II) ions with NaY in water solution, (ii) reaction of Cu(II)–NaY with excess 1,3-bis(2-carboxyaldehydephenoxy)propane (O_2O_2) in methanol, [(1,3-bis(2-carboxyaldehydephenoxy)propane)copper]$^{2+}$@NaY, [Cu(O_2O_2)]$^{2+}$@NaY (iii) template synthesis of [Cu(O_2O_2)]$^{2+}$@NaY with diamine. The obtained new complex nanoparticles entrapped in the nanopores of zeolite Y have been characterized by elemental analysis FT-IR, XPS, DRS, UV–vis spectroscopic techniques, molar conductance, magnetic moment data, XRD and nitrogen adsorption. Analysis of data indicates all of the complexes have been encapsulated within nanopores without affecting the zeolite framework structure.

Complex nanoparticles entrapped in the nanopores of zeolite Y are fascinating class of materials, which have attracted wide spread attention in basic science as well as technology development. Zeolites are endowed with unique physical and chemical characterization, which offers opportunities to manipulate active site microenvironment. They are even compared with the catalytic antibodies and metallo-enzymes and hence they are often referred to as zeozymes [1,2]. Some of the prominent physical characteristics of zeolites are their ruggedness to temperature and pressure and their ability to recognize, discriminate and organize molecules with less than 0.1 nm levels precision at the active site [3]. Moreover, non corrosive, environment friendly and economically viable nature of the zeolite catalyzed reactions have provided the opportunity for the development of various industrial processes such as fluid catalytic cracking, hydrocracking, isomerization and oxidation. Zeolites are crystalline aluminosilicates whose internal voids are formed by cavities and channels of strictly regular dimensions and of different sizes and shapes. In particular, the pore structure of Y zeolite consists of almost spherical 1.3 nm cavities interconnected tetrahedrally through smaller apertures of 0.74 nm diameter. The metal complex can be easily accommodated inside the supercages of Y zeolite. Over the last decade, there has been a dramatic increase in synthesis, characterization and application of novel nanoporous materials [4–18].

In the continuation of previous works, I decided to prepare 15- and 16-membered diaza dioxa macrocyclic ligand encapsulated within nanopores of zeolite-Y. To the best of my knowledge, this is the first report about synthesis of encapsulated 15- and 16-membered diaza dioxa macrocyclic ligand. In this research, has been shown that the macrocyclic complexes can be synthesized via two steps within nanopores of zeolite-Y. With this applied strategy, other macrocyclic compound could be encapsulated within zeolite-Y.

In this paper, has been reported the synthesis and characterization of copper(II) complexes of 15- and 16-membered diaza dioxa macrocyclic ligand "Et[15]N_2O_2: 5,6,7,8,15,16-hexahydro-14H-dibenzo[b,h][1,10,4,7]dioxadiazacyclotridecine, Pr[16]N_2O_2: 7,8,15,16,17,18-hexahydro-6H,14H-dibenzo[b,I][1,11,4,8]dioxadiazacyclotetradecine, Ph[15]N_2O_2: 5,12,13,19-tetrahydro-11H-tribenzo[b,e,h][1,10,4,7]dioxadiazacyclotridecine, Ch[15]N_2O_2: 1,2,3,4,4a,5,12,13,19,19a-decahydro-11H-tribenzo[b,e,h][1,10,4,7]dioxadiazacyclotridecine" encapsulated within the nanopores of zeolite-Y by the template condensation of diamine and [(1,3-bis(2-carboxyaldehydephenoxy)propane)copper]$^{2+}$, [Cu(R[15 or 16] N_2O_2)]$^{2+}$@NaY, shown in Schemes 1 and 2. Instrumental details for elemental analysis, IR, TGA, XRD, XPS, BET spectroscopy were the same as described earlier [19–22].

[Cu(R[15]N_2O_2)]$(ClO_4)_2 \cdot 2H_2O$ and copper(II) complex nanoparticles entrapped in the nanopores of zeolite Y, [Cu(R[15 or

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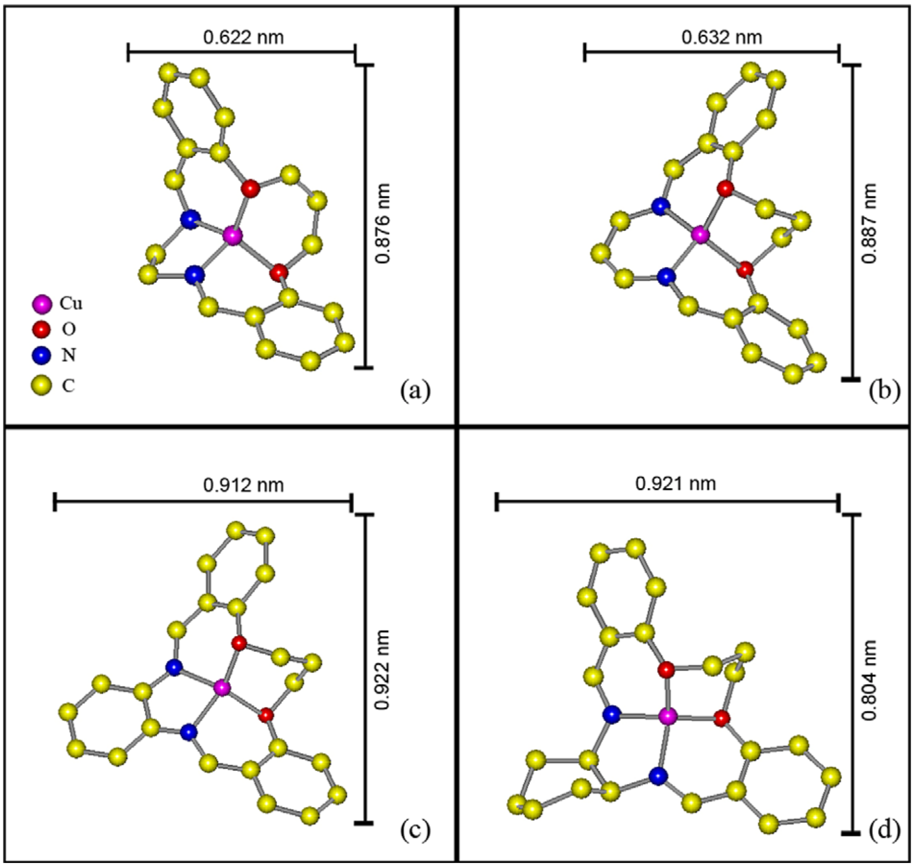
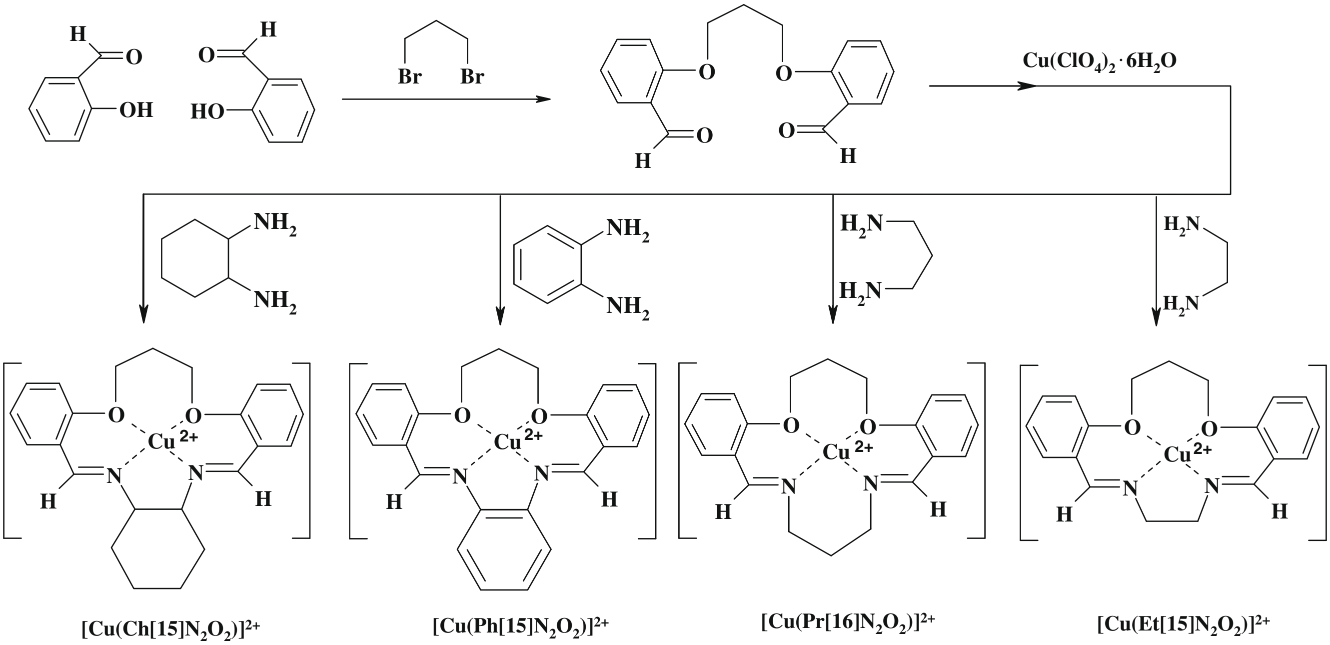


Scheme 1. 15-, and 16-membered diaza dioxa macrocyclic copper(II) complexes.



Scheme 2. Reaction mechanism of 15-, and 16-membered diaza dioxa macrocyclic copper(II) complexes.

$16]N_2O_2)]^{2+}$@NaY (R = Et, Pr, Ph, Ch) were prepared according to Ref. [23]. In this study, the [1 + 1] macrocycle Schiff-base complexes were prepared as the major product by the reaction dialdehyde and copper(II) perchlorate with diamines in methanol. The macrocyclic complexes were characterized by elemental analysis, mass and FT-IR spectrometry. The mass spectrum of complexes plays an important role in confirming the monomeric [1 + 1] (dialdehyde and diamine) nature of complexes [34]. All mass spectra showed molecular ion peaks for the 1:1 metal-to-ligand stoichiometry with no further peaks above them. The copper(II) complexes are extremely stable in the solid state and in the solution media, these complexes are relatively stable against ligand dissociation in highly acidic solution. The crystals were unsuitable for single-crystal X-ray structure determination and are insoluble in most common solvents, including water, EtOH, Et_2O, CH_3Cl, CH_2Cl_2, $C_2H_5OOCCH_3$, and CH_3CN.

A preliminary identification of the copper complexes was made on the basis of their IR spectra, which exhibited no bands characteristic of free primary amine, thus supporting the proposed macrocyclic skeleton (Scheme 1). The copper(II) complexes, $[Cu(R[15 \text{ or } 16]N_2O_2)](ClO_4)_2$, readily dissolve in DMF and DMSO. The overall geometries of all macrocycles have been deduced on the basis of the observed values of the magnetic moments and the band positions in the electronic spectra [34]. Magnetic studies and conductivity measurements. The metal-ligand mole ratio was found to be 1:1, according to elemental analysis. Since all of the copper(II) complexes are paramagnetic, their NMR spectra could not be obtained. Magnetic susceptibility measurements provide sufficient data to characterize the structure of the metal complexes. The copper(II) complexes are 2:1 electrolytes as shown by their molar conductivities (Λ) in DMF at 10^{-3} M, which are in the range 170–180 Ω^{-1} cm^2 mol^{-1}. The molar conductivities of the compounds in DMF are the range reported for 2:1 electrolytes (Scheme 2).

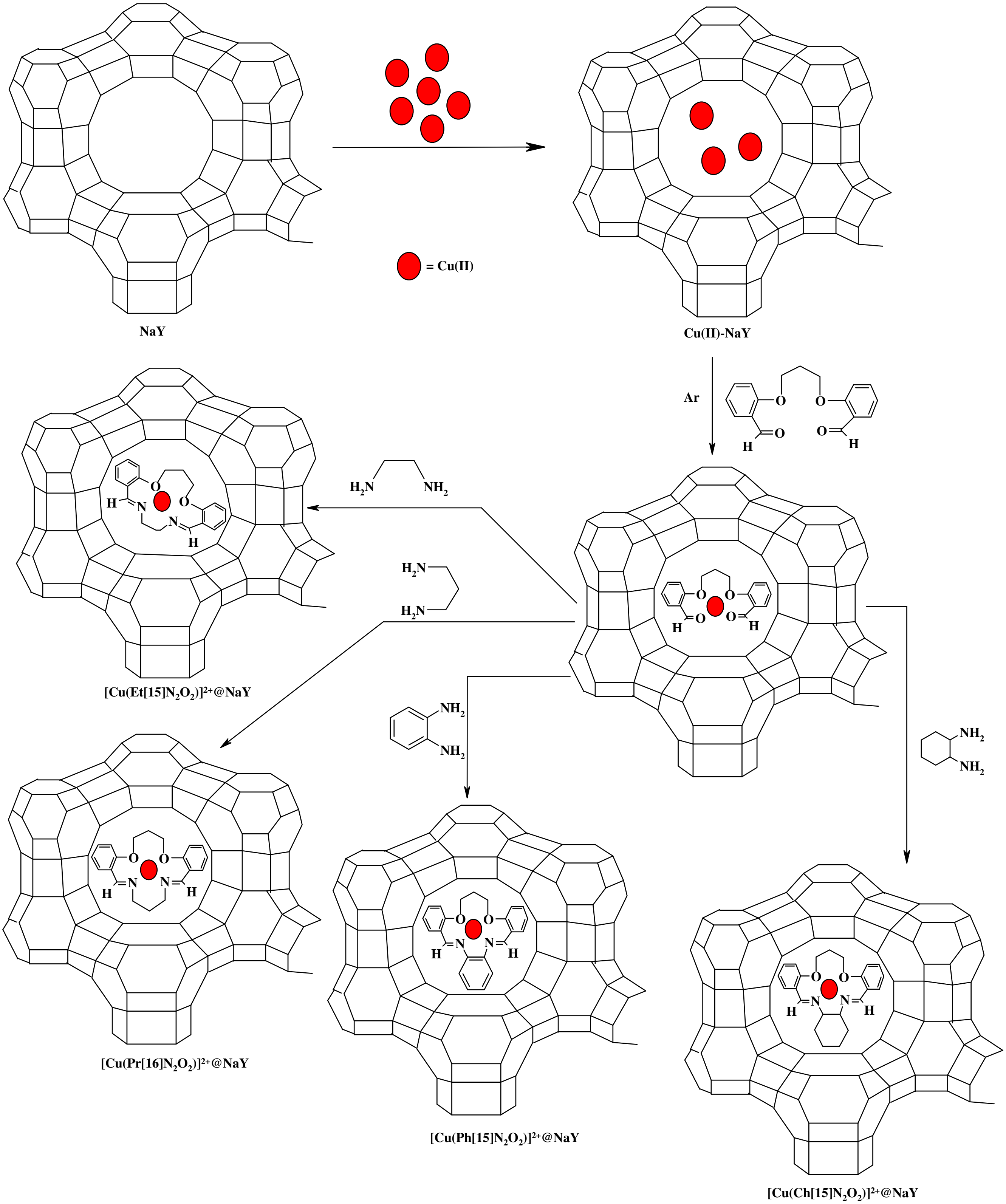
The percentage of copper contents determined before and after encapsulation by inductively coupled plasma (ICP) along with their expected formula is presented [34]. As crude mass was extracted with methanol, the metal ion content found after encapsulation is only due to the presence of metal complexes in the nanopores of the zeolite-Y. The molecular formula of the complex nanoparticles are based on the neat complexes $[Cu(R[15 \text{ or } 16]N_2O_2)]^{2+}$ that have also been prepared and characterized. Synthesis of copper(II) complex nanoparticles encapsulated in the nanopores of zeolite-Y involves three steps: (i) exchange of Co(II) ions with NaY in water solution, (ii) reaction of Cu(II)–NaY with excess dialdehyde (O_2O_2) in methanol (iii) reaction of $[Cu(O_2O_2)]^{2+}$–NaY with diamine (1,2-diaminoethane, 1,3-diaminopropane, 1,2-diaminobenzene or 1,2-diaminocyclohexane) where diamine slowly enters into the nanopores of zeolite-Y due to its template nature and interacts with $[Cu(O_2O_2)]^{2+}$ ions (Scheme 3). Soxhlet extraction using ethanol and chloroform finally purified the impure complexes. The remaining un-complexed metal ions in zeolite were removed by exchanging with aqueous 0.01 M NaCl solution. As one extra anionic ligand would be required to balance the overall charges on the Cu(II), Cl^- of NaCl used during exchanged process fulfills this requirement. Thus, the formula of copper(II) complex may be written as $[Cu(R[15 \text{ or } 16]N_2O_2)]^{2+}$@NaY. The parent NaY zeolite has Si/Al molar ratio of 2.53 which corresponds to a unit cell formula $Na_{56}[(AlO_2)_{56}(SiO_2)_{136}]$. The unit cell formula of metal-exchanged zeolites shows 10.8 moles of copper dispersion per unit cell ($Na_{34}Co_{10.8}[(AlO_2)_{56}(SiO_2)_{136}]\cdot nH_2O$). Metal ion exchange at around 36% leads to 2.81–2.87% of metal loading in zeolite. The CHN analysis results of the neat copper complexes showed near similarity to the theoretical values. The copper contents of the zeolite encapsulated samples were estimated by dissolving known amounts of the catalyst in concentric HCl and using AAS. The analytical data of each complex indicate molar ratios of Cu:C:H almost close to those calculated for the mononuclear structure [34].

FT-IR spectra of copper(II) complexes were recorded in KBr pellet from 4000 to 400 cm^{-1}. The infrared spectra of copper(II) complexes have been studied in order to characterize their structures. The broad bands within the ~3334 cm^{-1} range for all copper(II) complexes can be attributed to stretching vibrations of water molecule $\upsilon(H_2O)$ [24]. A strong band observed in the IR spectra of the copper(II) complexes in the ~1615 cm^{-1} region which is attributed to the υ(C=N) stretch, indicating coordination of the azomethine nitrogen to copper metal [25]. Coordination of the Schiff-base of compounds to the copper(II) center through the two nitrogen and two oxygen atoms (N_2O_2) are expected to reduce the electron density in the azomethine link and hydroxyl group. The spectra of all the copper(II) complexes are dominated by bands between ~2940 cm^{-1} due to υ(Alph.–CH) groups. A new band appearing in the ~1194 cm^{-1} region was assigned to υ(R–O) mode [26]. The stretching vibrations υ(Ar–C=C) show a very strong band in the 1490–1490 and 1456–1458 cm^{-1} range. Conclusive evidence of the bonding is also shown by the observation that new bands in the IR spectra of the copper(II) complexes appear at ~460 cm^{-1} and ~350 cm^{-1} assigned to υ(Cu–O) and υ(Cu–N) stretching vibrations. Thus, from the IR spectra it is clear that the compounds are bonded to the copper ion in a tetradentate fashion through the deprotonated phenolate oxygen and aldimine nitrogen (Scheme 1). Also, infrared spectra of the copper(II) complexes exhibit an intense band approximately between 1182 and 1110 cm^{-1} along with a weak band at between 651 and 625 cm^{-1} which have been assigned to the perchlorate complexes due to υ(Cl–O) of uncoordinated perchlorate anions [27]. The IR bands of all encapsulated complex nanoparticles were weak due to their low concentration in the zeolite. Cu(II) complex nanoparticles encapsulated in the zeolite cages did not show any significant shift in C=N stretching modes. We did not notice any appreciable changes in the frequencies of copper(II) complexes after incorporation into zeolite matrix.

The UV–vis spectral data for the metal complexes are given in Experimental section. The electronic spectra of copper(II) complexes in DMF show four peaks in the UV–vis. region. The absorption bands below 290 nm are practically identical and can be attributed to $\pi \rightarrow \pi^*$ transitions in the benzene ring and azomethine groups. The absorption bands observed within the ~335 nm are most probably due to the transitions of $n \rightarrow \pi^*$ of imine groups [28]. The general character of these spectra is very similar to that of the corresponding complexes of unsymmetrical disubstituted phenoxy groups. This is probably due to the fact that metal-to-ligand charge transfer and ligand-to-metal charge transfer transitions have similar energy differences [29]. The visible spectra of the $[Cu(R[15 \text{ or } 16]N_2O_2)]^{2+}$ complex consists of a maximum or a broad shoulder around 608 nm, which can be assigned to the $^2E \rightarrow {}^2T_2$. The magnetic moment for the former complex is 1.93 μB, which may be due to either tetrahedral or square planar structure [30,31]. The diffuse reflectance spectra of copper(II) complexes contain diaza dioxa macrocycle were almost identical before and after encapsulation, indicating the complexes maintain their geometry even after supported without significant distortion. These data compare closely with that of pure complexes as well as of encapsulated complexes and are indicative of a tetrahedral structure present within the nanodimensional pores of zeolite.

The X-ray diffraction (XRD) patterns of encapsulated complexes are shown in Fig. 1. The encapsulated complex exhibit similar peaks to those of zeolite Y, except for a slight change in the intensity of the peaks, no new crystalline pattern emerges. These facts confirmed that the framework and crystallinity of zeolite were not destroyed during the preparation, and that the complexes were well distributed in the cages. The relative peak intensities of the 220, 311 and 331 reflections have been thought to be correlated to the locations of cations. In zeolite Y, the order of peak intensity is in the order: $I_{331} \gg I_{220} > I_{311}$, while in encapsulated complexes, the order of peak intensity became $I_{331} \gg I_{311} > I_{220}$. The difference indicates that the ion-exchanged Cu^{2+}, which substitutes at the location of Na^+, undergoes rearrangement during complexation.

The surface area and pore volume of the materials are studied [34]. The encapsulation of $[Cu(R[15 \text{ or } 16]N_2O_2)]^{2+}$ complexes in zeolite reduced the adsorption capacity and the surface area of the zeolite. The lowering of the pore volume and surface area indicated the presence of complexes within the zeolite nanocages and not on the external surface.



Scheme 3. Encapsulation of copper(II) complex nanoparticles of 15-, and 16-membered diaza dioxa Schiff-base within nanopores of zeolite-Y.

Thermal stability of as-prepared compound was investigated by thermogravimetric analysis (TGA). The thermal decomposition of all these materials such as: $[Cu(R[15 \text{ or } 16]N_2O_2)]^{2+}$@NaY occurs in two steps (see Fig. 2). First step starts shortly after increasing the temperature above 150 °C and continues until the loss of all intrazeolite water. Second step occurs in a wide temperature range (200–450 °C) and is due to the slow decomposition of the chelating ligand. A very small weight percentage loss indicates the presence of only small amount of metal complex insertion in the nanopores of the zeolite. This is in agreement with the low percentage of me-

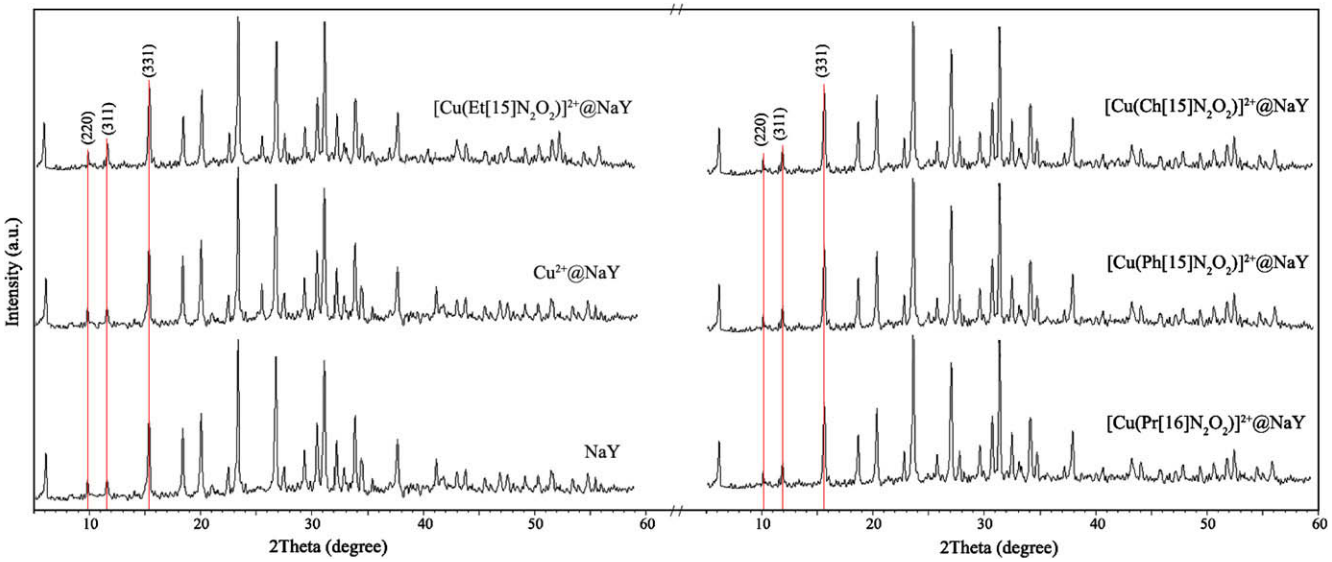


Fig. 1. XRD patterns of NaY, Cu^{2+}@NaY, $[Cu(Et[15]N_2O_2)]^{2+}$@NaY, $[Cu(Pr[16]N_2O_2)]^{2+}$@NaY, $[Cu(Ph[15]N_2O_2)]^{2+}$@NaY and $[Cu(Ch[15]N_2O_2)]^{2+}$@ NaY.

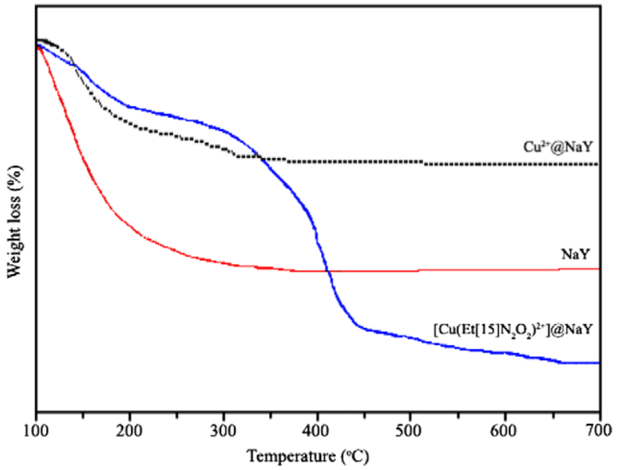


Fig. 2. TGA profiles of NaY, Cu^{2+}@NaY and $[Cu(Et[15]N_2O_2)]^{2+}$@NaY.

tal content estimated by atomic absorption spectrometer. Compared to the neat complex, the decomposition of the zeolite-encapsulated complex nanoparticles occurs at the higher temperature. A similar enhancement of the thermal stability of a metal complex on encapsulation has been observed earlier [32].

The presence of the complex in NaY was supported by XPS analysis. All modified NaY samples revealed the presence of oxygen, sodium, silicon and aluminium from the zeolite lattice in their XPS resolution spectra. The bands typical of the copper(II) complex, scarcely visible because of their low loading, were identified in the Cu $2p_{3/2}$ and N 1s region. The bulk and the surface Si/Al atomic ratios of NaY and of modified samples were similar, which indicates that de-alumination does not occur during the encapsulation procedure. The binding energies of the elements detected by XPS are summarized. The most intense bands identified are due to the zeolite structure, in the Si 2p region a band at 103.5 eV typical for Si atoms with different chemical environments, such as SiO_4 and terminal Si–OH groups. In the Al 2p region a band at 75.1 eV from the tetrahedral AlO_4 groups and a symmetrical large band at 531.0 eV from the O 1s region, and finally a band in the Na 1s region at 1072.6 eV were also observed [34]. The amount of surface copper is very similar to the bulk copper content, which that suggests the complex nanoparticles are homogeneously distributed throughout the NaY crystals. The medium binding energy values for Cu $2p_{3/2}$ are different before and after encapsulation, which indicates the change in environment of the copper upon coordination with the macrocyclic ligand. Before coordination the medium binding energy of Cu $2p_{3/2}$ value is 934.0 eV (Cu(II)@NaY) and after the complex encapsulation the value is 935.8 eV, $[Cu(Et[15]N_2O_2)]^{2+}$@NaY, 935.6 eV, $[Cu(Pr[16]N_2O_2)]^{2+}$@NaY, 936.1 eV, $[Cu(Ph[15]N_2O_2)]^{2+}$@NaY and 935.9 eV, $[Cu(Ch[15]N_2O_2)]^{2+}$@NaY (Table 1). These results confirm the same copper coordination sphere for the complex when free or encapsulated within NaY zeolite and that the host matrix environment does not affect the valence state of the metal atom of the complex. The high resolution C 1s spectrum of encapsulated complexes shows an asymmetric band centered at 285.0 eV that can be de-convoluted into three individual bands. The three bands at high energy were also observed in the starting material and are presumably due to the presence of some contamination. The band at 289.1 eV is attributed to the aromatic carbons ligand. The encapsulated complexes and the free complex samples exhibit in the N 1s region a band centered at

Table 1
XPS data of NaY, Cu@NaY, $[Cu(Et[15]N_2O_2)]^{2+}$@NaY, $[Cu(Pr[16]N_2O_2)]^{2+}$@NaY, $[Cu(Ph[15]N_2O_2)]^{2+}$@NaY and $[Cu(Ch[15]N_2O_2)]^{2+}$@ NaY.

Sample	Si(2p) (eV)	Al(2p) (eV)	Na(1s) (eV)	C(1s) (eV)	O(1s) (eV)	Si/Al (eV)	Cu $2p_{3/2}$ (eV)
NaY	103.5	75.1	1072.6	285.0	531.0	2.61	–
Cu@NaY	103.5	75.1	1072.6	285.0	532.5	2.58	934.0
$Cu(Et[15]N_2O_2)]^{2+}$@NaY	103.6	75.1	1072.6	285.0	532.7	2.58	935.8
$[Cu(Pr[16]N_2O_2)]^{2+}$@NaY	103.6	75.1	1072.7	285.0	532.8	2.58	935.6
$[Cu(Ph[15]N_2O_2)]^{2+}$@NaY	103.6	75.1	1072.8	285.0	532.9	2.58	936.1
$[Cu(Ch[15]N_2O_2)]^{2+}$@NaY	103.6	75.1	1072.7	285.0	532.7	2.58	935.9

400.6, due to the contribution of nitrogen atoms of the ligand. Copper remains in the 2+ oxidation state in encapsulated complexes and it matches well with the reported values for similar systems [33].

In summary, the diaza dioxa macrocyclic complex nanoparticles, $[Cu(R[15\text{ or }16]N_2O_2)]^{2+}$ (R = Et, Pr, Ph, Ch), have been encapsulated in the nanopores of zeolite by template condensation between pre-entrapped, $[Cu(O_2O_2)]^{2+}$@NaY (O_2O_2 = [1,3-bis(2-carboxyaldehydephenoxy)propane)] complex with diamine, $[Cu(N_2O_2\text{-}N)_2]^{2+}$@NaY. This strategy appears to be effective for the encapsulated of Cu(II) complexes with 15-, 16-membered diaza dioxa macrocycle ligands derived from $[CuO_2O_2]^{2+}$@NaY, as template condensation in the nanopores is still possible and no unreacted $[CuO_2O_2]^{2+}$ ions was detected. Furthermore, the spectroscopic data suggest that the encapsulated complex nanoparticle experience very little distortion in the supercage and that the chemical ligation to the zeolite surface is minimal. The new complex nanoparticles entrapped in the nanopores of zeolite Y "$[Cu(R[15]N_2O_2)]^{2+}$@NaY (R = Et, Pr, Ph, Ch)" were characterized by several techniques: chemical analysis and spectroscopic methods (FT-IR, UV/vis, XRD, BET, DRS, XPS). The Cu(II) complex nanoparticles are proposed to exhibit tetrahedral geometry.

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[23] *Preparation of [1,3-Bis(2-carboxyaldehydephenoxy)propane] (dialdehyde):* Dialdehyde was prepared by refluxing a mixture of 2-hydroxybenzaldehyde (4.0 g, 30 mmol), 1,3-dibromopropane (1.5 ml, 15 mmol) and K_2CO_3 (4.1 g, 30 mmol) in dry acetone (30 ml). After the completion of the reaction (18 h), the acetone was evaporated under vacuum and the resulting solid washed with water to extract the formed KBr. The crude solid product was then recrystallized from 95% ethanol to afford pure 1,3-Bis(2-carboxyaldehydephenoxy)propane in 55% yield: m.p. 125–129 °C, IR (KBr) υ_{max} 2952, 1701, 1600, 1462, 1243 and 1158 cm^{-1}, ^1H NMR (DMSO-d_6, 400 MHz) d 9.86 (s, 2H), 7.93 (d, 8.9 Hz, 4H), 7.23 (d, 8.8 Hz, 4H), 4.40 (t, 6.5 Hz, 4H) and 2.3 (quintet, 6.3 Hz, 2H), ^{13}C NMR (DMSO-d_6, 80 MHz) d 190.5, 162.7, 131.2, 129.1, 114.6, 64.2 and 27.6.*Preparation of $[Cu(R[15\text{ or }16]N_2O_2)](ClO_4)_2{\cdot}2H_2O$ (R = Et, Pr, Ph, Ch):* To a stirred solution of dialdehyde (1.40 g, 5 mmol) and $Cu(ClO_4)_2{\cdot}6H_2O$ (1.85 g, 5 mmol) in MeOH (60 ml) was added dropwise various diamines (5 mmol) in MeOH (40 ml). After the addition was completed, the stirring was continued for 2 h. Then the precipitate was filtered and washed with MeOH and dried in air. The products were crystallized from hot methanol.*Preparation of [Cu(dialdehyde)]$^{2+}$@NaY ($[Cu(O_2O_2)]^{2+}$@NaY):* A 2 g NaY zeolite was suspended in 100 ml distilled water, which contained $Cu(ClO_4)_2{\cdot}6H_2O$ (0.025 M). The mixture was then heated while stirring at 90 °C for 24 h. The solid was filtered, washed with hot distilled water till the filtrate was free from any copper(II) ion (by AAS of filtrate) content and dried for 10 h at 80 °C under vacuum. The ionic exchange degree was determined by atomic absorption spectrophotometer. Typically a 4 g sample of Cu(II)–NaY zeolite was mixed with 1.60 g of [1,3-bis(2-carboxyaldehydephenoxy)propane] suspended in 100 ml of methanol and then refluxed for 8 h. The solid consisting of dialdehyde coordinated with Cu(II) in Cu(II)–NaY and denoted as $[Cu(O_2O_2)]^{2+}$@NaY was collected by filtration, washed with methanol. The resulted zeolites, were Soxhlet extracted with chloroform (for 4 h) and then with ethanol (for 3 h) to remove excess unreacted dialdehyde and any copper(II) complexes adsorbed onto the external surface of the zeolite crystallines. The resulting solids were dried at 70 °C under vacuum for 24 h.*Preparation of complex nanoparticles entrapped in the nanopores of zeolite Y:* To a stirred methanol suspension (100 ml) of $[Cu(O_2O_2)]^{2+}$@NaY (2 g) were slowly added diamine, 1,2-diaminoethane, 1,3-diaminopropane, 1,2-phenylenediamine and 1,2-diaminocyclohexane, (under Ar atmosphere). The mixture was heated under reflux condition for 24 h. The solution was filtered and the resulting zeolites, were Soxhlet extracted with chloroform (for 4 h) and then with ethanol (for 4 h) to remove excess unreacted products from amine-aldehyde condensation and any copper(II) complexes adsorbed onto the external surface of the zeolite crystallites. The resulting solids were dried at 70 °C under vacuum for 12 h. The remaining $[Cu(O_2O_2)]^{2+}$ ions in zeolite were removed by exchanging with aqueous 0.1 M NaCl solutions. The stability of the encapsulated complex nanoparticles was checked after the reaction by UV–vis and possible leaching of the complex was investigated by UV–vis in the reaction solution after filtration of the zeolite. The amounts of Cu(II) complexes encapsulated in zeolite matrix were determined by the elemental analysis and by subtracting the amount of Cu(II) complex left in the solutions after the synthesis of the materials as determined by UV–vis spectroscopy, from the amount taken for the synthesis.

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[34] Chemical composition (experimental found are given in parentheses), IR stretching frequencies, conductive electrical, magnetic momentum, UV. Vis and mass data of neat and zeolite-encapsulated copper(II) complex nanoparticles: Anal. Calc. for $[Cu(Et[15]N_2O_2)](ClO_4)_2$: C: 37.61 (37.46), H: 3.99 (3.86), N: 4.62 (4.75), C/N: 8.14 (7.89), Cu: 10.47 (10.23), Λ_M (DMF): 180 $\Omega^{-1}\,cm^2\,mol^{-1}$, IR data (KBr, ν cm^{-1}): $\nu(H_2O)$: 3334, ν(Ar–CH): 3070, ν(Alph.–CH): 2940, 2873, ν(C=N): 1615, $\nu(ClO_4^-)$: 1110, 532, ν(Substituted benzene): 758, ν(Cu–O): 460, ν(Cu–N): 350, μ_{eff} (B.M): 1.93, UV–vis (λ_{max}, nm) (DMF): 240, 271, 328, 611, Mass spectra: *m/z*: 570, $\{[Cu(Et[15]N_2O_2)](ClO_4)_2\}\text{–}2H_2O\text{–}H]^+$, 470, $\{[Cu(Et[15]N_2O_2)](ClO_4)\}\text{–}ClO_4\text{–}2H_2O\text{–}H]^+$, 371,$\{[Cu(Et[15]N_2O_2)]\}\text{–}2ClO_4\text{–}2H_2O\text{–}H]^+$. Anal. Calc. for $[Cu(Pr[16]N_2O_2)](ClO_4)_2$: C: 38.69 (38.52), H: 4.22 (4.17), N: 4.51 (4.69), C/N: 8.58 (8.21), Cu: 10.23 (10.11), Λ_M (DMF): 175 $\Omega^{-1}\,cm^2\,mol^{-1}$, IR data (KBr, ν cm^{-1}): $\nu(H_2O)$: 3340, ν(Ar–CH): 3052, ν(Alph.–CH): 2941, 2872, ν(C=N): 1613, $\nu(ClO_4^-)$: 1110, 532, ν(Substituted benzene): 758, ν(Cu–O): 461, ν(Cu–N): 355, μ_{eff} (B.M): 1.95, UV–vis (λ_{max}, nm) (DMF): 240, 271, 328, 613, Mass spectra: *m/z*: 584, $\{[Cu(Et[15]N_2O_2)](ClO_4)_2\}\text{–}2H_2O\text{–}H]^+$, 484, $\{[Cu(Et[15]N_2O_2)](ClO_4)\}\text{–}ClO_4\text{–}2H_2O\text{–}H]^+$, 385,$\{[Cu(Et[15]N_2O_2)]\}\text{–}2ClO_4\text{–}2H_2O\text{–}H]^+$. Anal. Calc. for $[Cu(Ph[15]N_2O_2)](ClO_4)_2$: C: 42.18 (42.03), H: 3.69 (3.54), N: 4.28 (4.38), C/N: 9.86 (9.59), Cu: 9.70 (9.53), Λ_M (DMF): 170 $\Omega^{-1}\,cm^2\,mol^{-1}$, IR data (KBr, ν cm^{-1}): $\nu(H_2O)$: 3350, ν(Ar–CH): 3075, ν(Alph.–CH): 2944, ν(C=N): 1624, $\nu(ClO_4^-)$:1110, 532, ν(Substituted benzene): 758, ν(Cu–O): 468, ν(Cu–N): 361, μ_{eff} (B.M): 1.96, UV–vis (λ_{max}, nm) (DMF): 240, 271, 328, 609, Mass spectra: *m/z*: 618, $\{[Cu(Et[15]N_2O_2)](ClO_4)_2\}\text{–}2H_2O\text{–}H]^+$, 519, $\{[Cu(Et[15]N_2O_2)](ClO_4)\}\text{–}ClO_4\text{–}2H_2O\text{–}H]^+$, 420,$\{[Cu(Et[15]N_2O_2)]\}\text{–}2ClO_4\text{–}2H_2O\text{–}H]^+$. Anal. Calc. for $[Cu(Ch[15]N_2O_2)](ClO_4)_2$: C: 41.80 (41.69), H: 4.57 (4.43), N: 4.24 (4.36), C/N: 9.86 (9.56), Cu: 9.61 (9.49), Λ_M (DMF): 173 $\Omega^{-1}\,cm^2\,mol^{-1}$, IR data (KBr, ν cm^{-1}): $\nu(H_2O)$: 3342, ν(Ar–CH): 3066, ν(Alph.–CH): 2876, ν(C=N): 1620, $\nu(ClO_4^-)$:1110, 532, ν(Substituted benzene): 758, ν(Cu–O): 466, ν(Cu–N): 354, μ_{eff} (B.M): 1.99, UV–vis (λ_{max}, nm) (DMF): 240, 271, 328, 610, Mass spectra: *m/z*: 624, $\{[Cu(Et[15]N_2O_2)](ClO_4)_2\}\text{–}2H_2O\text{–}H]^+$, 524, $\{[Cu(Et[15]N_2O_2)](ClO_4)\}\text{–}ClO_4\text{–}2H_2O\text{–}H]^+$, 425,$\{[Cu(Et[15]N_2O_2)]\}\text{–}2ClO_4\text{–}2H_2O\text{–}H]^+$. NaY: Si: 21.48, Al: 8.50, Na: 3.28, Si/Al: 2.53, Surface area: 545 m^2/g, pore volumen: 0.31 ml/g, Anal. Calc. for Cu(II)–NaY: Si: 21.53, Al: 8.53, Na: 3.36, Co: 3.71, Si/Al: 2.53, Surface area: 532 m^2/g, pore volumen: 0.30 ml/g, $[Cu(Et[15]N_2O_2)]^{2+}$@NaY: C: 10.80, H: 1.19, N: 1.36, Cu: 2.87, C/N: 7.94, Cu/N: 2.11, Si: 21.26, Al: 8.40, Na: 5.35, Si/Al: 2.53, Surface area: 475 m^2/g, pore volumen: 0.18 ml/g, DRS (λ_{max}, nm): 608, IR data (KBr, ν(C=N) cm^{-1}), 1612. $[Cu(Pr[16]N_2O_2)]^{2+}$@NaY: C: 11.12, H: 1.19, N: 1.33, Cu: 2.83, C/N: 8.36, Cu/N: 2.13, Si: 21.24, Al: 8.39, Na: 5.34, Si/Al: 2.53, Surface area: 473 m^2/g, pore volumen: 0.17 ml/g, DRS (λ_{max},

nm): 610, IR data (KBr, ν(C═N) cm^{-1}), 1610. [Cu(Ph[15]N_2O_2)]$^{2+}$@NaY: C: 12.60, H: 1.37, N: 1.30, Cu: 2.81, C/N: 9.69, Cu/N: 2.16, Si: 21.20, Al: 8.38, Na: 5.29, Si/Al: 2.53, Surface area: 457 m^2/g, pore volumen: 0.14 ml/g, DRS (λ_{max}, nm): 606, IR data (KBr, ν(C═N) cm^{-1}), 1620. [Cu(Ch[15]N_2O_2)]$^{2+}$@NaY: C: 12.54, H: 1.35, N: 1.29, Cu: 2.82, C/N: 9.72, Cu/N: 2.18, Si: 21.22, Al: 8.39, Na: 5.30, Si/Al: 2.53, Surface area: 457 m^2/g, pore volumen: 0.14 ml/g, DRS (λ_{max}, nm): 607, IR data (KBr, ν(C═N) cm^{-1}), 1617.