Template Synthesis and Characterization of Host (Nanocavity of Zeolite Y)-Guest ([Cu([18]aneN4S2)]$^{2+}$, [Cu([20]aneN4S2)]$^{2+}$, [Cu(Bzo2[18]aneN4S2)]$^{2+}$, [Cu(Bzo2[20]aneN4S2)]$^{2+}$) Nanocomposite Materials

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Copper(II) complexes with tetraoxo dithia tetraaza macrocyclic ligands; [18]aneN4S2: 1,4,10,13-tetraaza-5,9,14,18-tetraoxo-7,16-dithia-cyclooctadecane, [20]aneN4S2: 1,5,11,15-tetraaza-6,10,16,20-tetraoxo-8,18-dithia-cyclocosane, Bzo2[18]aneN4S2: dibenzo-1,4,10,13-tetraaza-5,9,14,18-tetraoxo-7,16-dithia-cyclooctadecane, Bzo2[20]aneN4S2: dibenzo-1,5,11,15-tetraaza-6,10,16,20-tetraoxo-8,18-dithia-cyclocosane; were entrapped in the nanopores of zeolite-Y by a two-step process in the liquid phase: (i) adsorption of [bis(diamine)copper(II)] (diamine = 1,2-diaminoethane, 1,3-diaminopropane, 1,2-diaminobenzene, 1,3-diaminobenzene); [Cu(N-N)2]$^{2+}$-NaY; in the nanopores of the zeolite, and (ii) in situ template condensation of the copper(II) precursor complex with thiodiglycolic acid. The obtained complexes and new host-guest nanocomposite materials: [Cu([18]aneN4S2)]$^{2+}$-NaY, [Cu([20]aneN4S2)]$^{2+}$-NaY, [Cu(Bzo2[18]aneN4S2)]$^{2+}$-NaY, [Cu(Bzo2[20]aneN4S2)]$^{2+}$-NaY: have been characterized by elemental analysis FT-IR, DRS and UV-Vis spectroscopic techniques, molar conductance and magnetic moment data, XRD and, as well as nitrogen adsorption. Analysis of data indicates all of the complexes have been encapsulated within nanopore of zeolite Y without affecting the zeolite framework structure.

Key Words: Nanocomposite materials, Zeolite encapsulation, Template, Copper(II), Macrocycle

Introduction

The design and synthesis of macrocyclic ligand having heteronucleating donor atoms has been increased significant interest. It offers exciting possibilities for creative minds to construct novel supramolecular assemblies that are capable of performing highly specific molecular functions.[1] The N-S donor macrocycles also have theoretical interest, as they are capable of furnishing an environment of controlled geometry and ligand field strength.[2] The precise molecular recognition between macrocyclic ligands and their guests provides a good opportunity for studying key aspects of supramolecular chemistry, which are also significant in a variety of disciplines including chemistry, biology, physics, medicine and related science and technology.[3] Chemically mixed donor macrocycles are important because of great versality as ligands due to presence of several potential donor atoms, their flexibility and ability to coordinate with several metal ions.[3]

Synthesis and characterization of most transition metal complexes with macrocyclic mixed donor ligands containing mixed donors of nitrogen, oxygen and sulfur has been studied.[4-16] However, most of them were polyaza macrocyclic ligands, and macrocyclic mixed donor ligands containing N-S in the nanopores of zeolite Y have not been to some extent reported to date. The term nanopore materials have been used for those porous materials with pore diameters of less than 100 nm. Many kinds of crystalline and amorphous nanoporous materials such as framework silicates and metal oxides, zeolites, pillared clays, nanoporous silicon, carbon nanotubes and related porous carbons have been described lately in the literature.[17] Nanoporous materials are exemplified by crystalline framework solids such as zeolites, whose crystal structure defines channels and cages, i.e. nanopores, of strictly regular dimensions. They can impart shape selectivity for both the reactants and products when involved in the chemical reactions and processes. The large internal surface area and void volumes with extremely narrow pore size distribution as well as functional centers homogeneously dispersed over the surface make nanoporous solids highly active materials. Over the last decade, there has been a dramatic increase in synthesis, characterization and application of novel nanoporous materials.[18,19]

Coordination geometry and properties of most transition metal complexes with polyaza macrocyclic ligands have been studied.[19] However, most of them were tetraaza macrocyclic ligands, and tetraoxo dithia tetraaza macrocyclic ligands containing four nitrogen and two sulfur atoms within the nanocavity of zeolite-Y have not been yet. We have been interested in the synthesis of various types of N4S2 macrocyclic complexes containing thiodiglycolic acid from template synthesis in nanodimensional pores of zeolite-Y. Metal template condensation reaction often provides selective routes toward products that are not obtainable in the absence of metal ions. The reactions are simple "one-pot reactions" cheap and high yielding.

In this project there are two different approaches, first to synthesize the complexes, ligands were synthesized and isolated, and the metallic salts were added to form desired products; second because of the steric hindrance of the ligands

Table 1. Elemental analysis, vibrations parameters and molecular ion peaks for ligands and N_4S_2 macrocyclic coppert(II) and zinc(II) complexes.

Complex	Calculated (Found)					IR (KBr, cm⁻¹)						FAB mass (m/z)	
	C (%)	H (%)	N (%)	C/N	M (%)	I	II	III	IV	ν_{N-H}	ν_{M-N}	$[Cu-ClO_4]^-$	$[Cu-2ClO_4]^{2+}$
[18]aneN4S2	41.4 (41.1)	5.8 (5.6)	16.1 (16.2)	2.6 (2.5)	-	1645	1572	1246	662	3205	-	-	-
[Cu([18]aneN4S2)](ClO4)2	23.6 (23.3)	3.3 (3.2)	9.2 (9.3)	2.6 (2.5)	10.4 (10.2)	1623	1575	1232	693	3270	440	511	412
[20]aneN4S2	44.7 (44.4)	6.4 (6.2)	14.9 (15.0)	3.0 (3.0)	-	1641	1570	1244	662	3200	-	-	-
[Cu([20]aneN4S2)](ClO4)2	26.3 (26.2)	3.8 (3.6)	8.8 (8.9)	3.0 (2.9)	9.9 (9.8)	1622	1573	1230	691	3250	438	539	439
Bzo2[18]aneN4S2	54.0 (53.9)	4.5 (4.4)	12.6 (12.8)	4.3 (4.2)	-	1650	1571	1248	661	3286	-	-	-
[Cu(Bzo2[18]aneN4S2)](ClO4)2	34.0 (33.8)	2.8 (2.6)	7.9 (8.1)	4.3 (4.2)	9.0 (8.8)	1630	1580	1235	697	3290	446	607	508
Bzo2[20]aneN4S2	54.08 (53.9)	4.5 (4.4)	12.6 (12.7)	4.3 (4.2)	-	1648	1571	1248	662	3284	-	-	-
[Cu(Bzo2[20]aneN4S2)](ClO4)2	34.0 (33.8)	2.8 (2.7)	7.9 (8.1)	4.3 (4.2)	9.0 (8.8)	1628	1580	1234	695	3282	445	607	508
[Zn([18]aneN4S2)](ClO4)2	23.5 (23.4)	3.3 (3.2)	9.1 (9.2)	2.6 (2.5)	10.7 (10.4)	1640	1567	1244	660	3160	403	-	-
[Zn([20]aneN4S2)](ClO4)2	26.2 (26.1)	3.8 (3.6)	8.7 (8.9)	3.0 (2.9)	10.2 (10.0)	1637	1570	1245	662	3150	405	-	-
[Zn(Bzo2[18]aneN4S2)](ClO4)2	33.9 (33.7)	2.8 (2.7)	7.9 (8.1)	4.3 (4.2)	9.2 (9.1)	1645	1571	1243	663	3100	407	-	-
[Zn(Bzo2[20]aneN4S2)](ClO4)2	33.9 (33.7)	2.8 (2.7)	7.9 (8.0)	4.3 (4.2)	9.2 (9.1)	1640	1570	1244	664	3100	409	-	-

which prevents complex passing through the 7 Å pore of zeolite Y. the "ship-in-a-bottle" method was used. In this paper. reported the synthesis and characterization of copper(II) complexes of 18- and 20-membered dithia tetraoxo tetraaza macrocyclic ligands: [18]aneN4S2: 1,4,10,13-tetraaza-5,9. 14,18-tetraoxo-7,16-dithia-cyclooctadecane. [20]aneN4S2: 1. 5,11,15-tetraaza-6,10,16,20-tetraoxo-8,18-dithia-cyclocosane. Bzo2[18]aneN4S2: dibenzo-1,4,10,13-tetraaza-5,9,14,18-tetrao-xo-7,16-dithia-cyclooctadecane, Bzo2[20]aneN4S2: dibenzo-1,5,11,15-tetraaza-6,10,16,20-tetraoxo-8,18-dithia-cyclocos-

ane: encapsulated within the nanopores of zeolite-Y by the template condensation of thiodiglycolic acid and [bis(diamine) copper(II)]; $[Cu([18]aneN_4S_2)]^{2+}$-NaY; $[Cu([20]aneN_4S_2)]^{2-}$-NaY; $[Cu(Bzo_2[18]aneN_4S_2)]^{2-}$-NaY; $[Cu([20]aneN_4S_2)]^{2-}$-NaY; shown in Scheme 1, 2.

Experimental

Materials. *Safety note*- perchlorate salt with organic ligands is often explosive and should be handled with caution. All
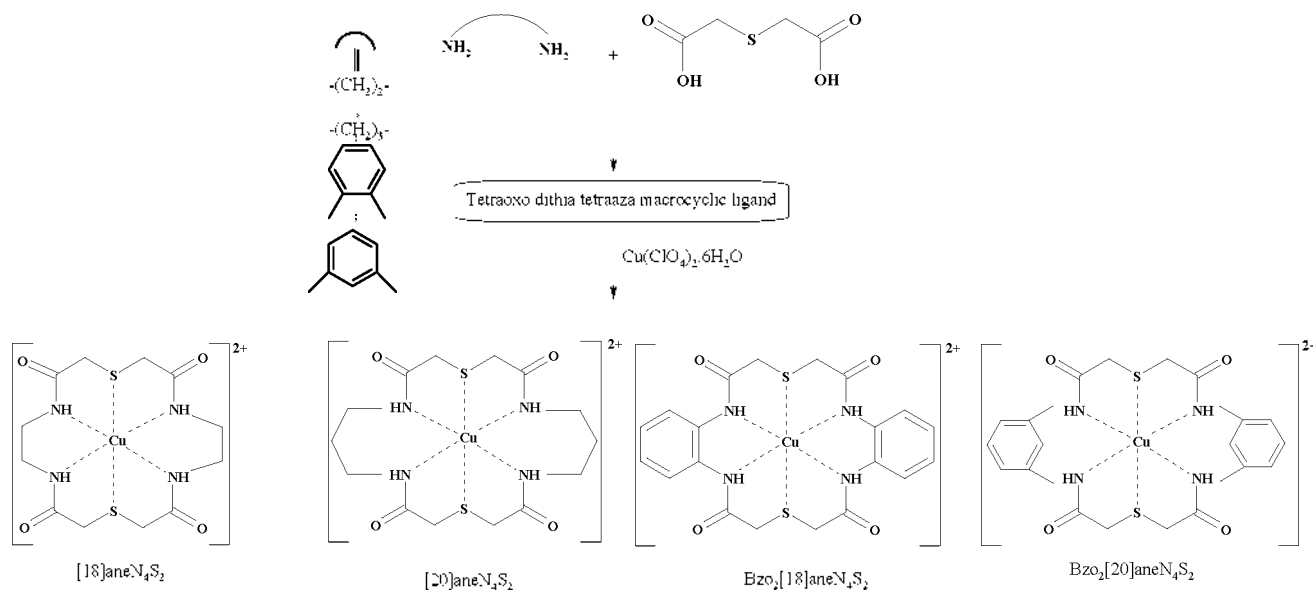
Scheme 1

other reagents and solvent were purchased from Merck (pro-analysis) and dried using molecular sieves (Linde 4Å). NaY with the Si:Al ratio of 2.53 was purchased from Aldrich (Lot No. 67812). Thiodiglycolic acid also obtained from Aldrich. 1.2-Diaminoethane. 1.3-diaminopropane. 1.2-diaminobenzene, and 1,3-diaminobenzene were obtained from Merck. Solvents were dried before used. The complex [Cu(N-N)2](ClO4)2 was prepared according to the published procedures.[20]

Physical measurements. Nitrogen adsorption measurements were performed at 77 K using a Coulter Omnisorb 100 CX instrument. The samples were degassed at 150 °C until a vacuum better than 10^{-3} Pa was obtained. Micropore volumes were determined by the *t*-method;[21,22] a "monolayer equivalent area" was calculated from the micropore volume as follows:[21] $S_{eq}.m^2 g^{-3} = (V_{micro} / V^1_M) \times N_A \times 0.162 \times 10^{-18}$, where V^1_M is the molar volume of liquid N_2, and N_A is the Avogadro constant. Atomic absorption spectra (AAS) were recorded on a Perkin-Elmer 4100-1319 Spectrophotometer using a flame approach, after the acid (HF) dissolves the known amounts of the zeolitic material. SiO_2 was determined by gravimetric analysis. Magnetic moments were calculated from magnetic susceptibility data obtained using a Johnson Matthey MK-1 magnetic susceptibility balance and conductance measurements with a Metrohm Herisau conductometer E 518. FT-IR spectra were recorded on Shimadzu Varian 4300 spectrophotometer in KBr pellets. The electronic spectra of the neat complexes were taken on a Shimadzu UV-vis scanning spectrometer (Model 2101 PC). Diffuse reflectance spectra (DRS) were registered on a Shimadzu UV/3101 PC spectrophotometer over the range 1500-200 nm, using MgO as reference. FAB mass spectra were recorded on a Kratos MS50TC spectrometer. The elemental analysis (CHN) of the materials was obtained from Carlo ERBA Model EA 1108 analyzer. XRD patterns were recorded by a Rigaku D-max C III. X-ray diffractometer using Ni-filtered Cu K$_α$ radiation.

Synthesis of tetraoxo dithia tetraaza macrocyclic ligand. Tetraoxo dithia tetraaza macrocyclic ligands ([18]aneN4S2. [20]aneN4S2. Bzo2[18]aneN4S2 or Bzo2[20]aneN4S2) were prepared by following the procedures reported in Ref.[23] The ligand has been synthesized by the condensation reaction of the thiodiglycolic acid (0.02 mol, 3.0 g) and diamine (0.02 mol); 1,2-diaminoethane (1.20 g), 1,3-diaminopropane (1.48 g), 1.2-diaminobenzene (2.16 g). 1.3-diaminobenzene (2.16 g). Both reagents were taken in equimolar ratio in a round bottom flask. in the presence of few drops of concentrated HCl (~pH 4-5) and were refluxed on a water bath up to the completion of reaction. After completion of the reaction the reaction mixture was kept in a refrigerator at 0 °C. over night. The cream colored crystals separated out. which were filtered, washed with cold ethanol and dried in vacuum over P_4O_{10}. The purity was checked by HPLC technique.

Preparation of [Cu([18 or 20]aneN4S2)](ClO4)2 and [Cu-(Bzo2[18 or 20]aneN4S2)](ClO4)2 complexes. Cu(ClO4)2 · 6H2O (10 mmol) dissolved in methanol (20 cm³) was reacted with an ethanol (20 cm³) solution of tetraoxo dithia tetraaza ligands ([18]aneN4S2. [20]aneN4S2. Bzo2[18]aneN4S2 or Bzo2[20]-

aneN4S2) (10 mmol) by refluxing for 1 h under nitrogen atmosphere. The mixture was heated at reflux for 6 h until a red solution resulted. The solution was cooled to room temperature and filtered to remove copper hydroxide. Excess lithium perchlorate dissolved in methanol was added to the filtrate, and the mixture was kept in the refrigerator until orange solid formed. The solids were filtered, washed thoroughly with cold ethanol and dried in vacuum.

Preparation of nanocomposite materials ([Cu([18 or 20]-aneN4S2)]²⁺-NaY and [Cu(Bzo2[18 or 20]aneN4S2)]²⁺- NaY). Typically a 4 g sample of NaY zeolite was mixed with 0.4 g of [bis(diamine)copper(II)] perchlorate : diamine = 1.2-diaminopropane. 1,3-diaminopropane, 1.2-diaminobenzene or 1,3-diaminobenzene; suspended in 100 cm³ of methanol and then refluxed for 8 h. The pale red solid consisting of [Cu(N-N)2]²⁺ exchanged with Na⁺ in NaY and denoted as [Cu(N-N)2]²⁺-NaY was collected by filtration. washed with ethanol. The resulted zeolites, were Soxhlet extracted with *N,N'*-dimethylformamide (for 4 h) and then with ethanol (for 3 h) to remove excess unreacted diamine and any Cu(II) complexes adsorbed onto the external surface of the zeolite crystallines. The resulting light orange solids were dried at 60 °C under vacuum for 24 h. To a stirred methanol suspension (100 cm³) of [Cu(N-N)2]²⁺-NaY (2 g) was slowly added thiodiglycolic acid (under N_2 atmosphere). The mixture was heated under reflux condition for 24 h until a red suspension resulted. The solution was filtered and the resulting zeolites. were Soxhlet extracted with *N,N'*-dimethylformamide (for 6 h) and then with ethanol (for 5 h) to remove excess unreacted products from amineester condensation and any copper(II) complexes adsorbed onto the external surface of the zeolite crystallines. The resulting red solids were dried at 70 °C under vacuum for 12 h. The remaining [bis(diamine) copper(II)] ions in zeolite were removed by exchanging with aqueous 0.1 M NaNO3 solutions. The stability of the encapsulated catalyst 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.

Results and Discussion

Copper(II) reacted with tetraoxo dithia tetraaza macrocyclic ligands in presence of LiClO4 to yield the cationic complexes: [Cu([18]aneN4S2)](ClO4)2. [Cu([20]aneN4S2)](ClO4)2. [Cu(Bzo2[18]aneN4S2)](ClO4)2 and [Cu(Bzo2[20]aneN4S2]-(ClO4)2. (Scheme 1). Elemental analysis and IR data have been given in Table 1. DMSO solutions of these complexes were conductive. Unfortunately. I could not grow any single crystals suitable for X-ray crystallographic studies. The molar conductance values (105-115 $Ω^{-1}$ mol^{-1} cm²) and measured of N4S2 macrocyclic complexes correspond to 1:2 electrolytes. Comparing the obtained magnetic measurement at room temperature and the results of electronic spectra (Table 2) of metal complexes with octahedral Cu(II) N4S2 macrocycle complexes indicated that the tetraoxo dithia tetraaza ligands of this study do not differ significantly from the tetraoxo dithia tetraaza ligands respect to the ligand field strength. The results of elemental analysis support the proposed macro-

Table 2. Magnetic moment, electronic spectral and molar conductance values of the N_4S_2 macrocyclic copper(II) complexes.[a]

Sample	$2B_{1g} \rightarrow 2B_{2g}$ nm, (ε, dm^{3}mol^{-1}cm^{-1})	$2B_{1g} \rightarrow 2E_g$ nm, (ε, dm^{3}mol^{-1}cm^{-1})	μ_{eff}(MB)	ΛM, Ω-1 cm^2 M-1
[Cu([18]aneN$_4$S$_2$)](ClO$_4$)$_2$	623.0 (200)	534.5 (85)	1.81	115
[Cu([20]aneN$_4$S$_2$)](ClO$_4$)$_2$	624.2 (220)	534.8 (84)	1.82	110
[Cu(Bzo$_2$[18]aneN$_4$S$_2$)](ClO$_4$)$_2$	613.5 (180)	529.1 (89)	1.80	106
[Cu(Bzo$_2$[20]aneN$_4$S$_2$)](ClO$_4$)$_2$	615.0 (190)	529.7 (93)	1.79	105

[a]In DMSO solutions.

Table 3. Chemical composition and IR stretching frequencies (as KBr pellets, cm^{-1}) of host (nanopores of zeolite) guest (N_4S_2 macrocyclic copper(II) complexes) nanocomposite materials.

| Sample	C (%)	H (%)	N (%)	C/N	Si (%)	Al (%)	Na (%)	Cu (%)	Si/Al	I	II	III	d→d (nm)
NaY	-	-	-	-	21.8	8.6	7.5	-	2.5	-	-	-	-
Cu(II)-NaY	-	-	-	-	21.5	8.5	3.3	3.9	2.5	-	-	-	-
[Cu([18]aneN$_4$S$_2$)]$^{2+}$-NaY	4.0	1.8	1.7	2.338	21.1	8.3	5.3	2.8	2.5	1633	1532	3215	621.5, 533.9
[Cu([20]aneN$_4$S$_2$)]$^{2+}$-NaY	4.1	1.8	1.5	2.8	21.1	8.3	5.3	2.8	2.5	1630	1527	3214	623.6, 534.2
[Cu(Bzo$_2$[18]aneN$_4$S$_2$)]$^{2+}$-NaY	4.3	1.8	1.1	4.0	21.0	8.3	5.3	2.8	2.5	1637	1536	3224	613.1, 528.5
[Cu(Bzo$_2$[20]aneN$_4$S$_2$)]$^{2+}$-NaY	4.3	1.8	1.1	4.0	21.0	8.3	5.2	2.7	2.5	1635	1533	3222	614.8, 529.9

cyclic structure. The proposed molecular formula of a macrocyclic Cu(II) compound was confirmed by the mass spectral analysis by comparing its molecular formula weight with m/z value. The mass spectra contain molecular ion peaks at m/z (M$^-$, M^{2+}): 511, 412 ([Cu([18]aneN$_4$S$_2$)](ClO$_4$)$_2$: 539, 439 [Cu([20]aneN$_4$S$_2$)](ClO$_4$)$_2$: 607, 508 [Cu(Bzo$_2$[18]aneN$_4$S$_2$)](ClO$_4$)$_2$: 607, 508 [Cu(Bzo$_2$[20]aneN$_4$S$_2$)](ClO$_4$)$_2$. These data

Figure 1. FT-IR spectra of (a) zeolite Na-Y, (b) [Cu([18]aneN$_4$S$_2$)](ClO$_4$)$_2$ and (c) [Cu([18]aneN$_4$S$_2$)]$^{2+}$-NaY.

are in good agreement with the respective molecular formula.

A preliminary identification of the metal 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 infrared spectra of the complexes (Table 1) does not exhibit any bands characteristic for the free -NH and -OH groups, and the appearance of four new bands characteristic of amide groups in the regions 1622-1630, 1573-1580, 1230-1235 and 691-697 cm^{-1}, assignable to amide **I** [υ(C=O)], amide **II** [υ(C-N) + δ (N-H)], amide **III** [δ(N-H)], and amide **IV** [o(C=O)] bands, respectively, which support the macrocyclic structure (Fig. 1). A single sharp band observed in the region 3250-3290 cm^{-1} may be assigned to υ(N-H) of the secondary amino group.[24] An important feature is the appearance of a new medium intensity band at ~445 cm^{-1} attributable to υ(M-N) which provide strong evidence for the involvement of nitrogen in coordination.[25]

The electronic spectra of the mononuclear copper complexes show two bands in the regions 529.1-534.8 and 613.5-624.2 nm, which can be assigned to $2B_{1g} \rightarrow 2E_g$ and $2B_{1g} \rightarrow 2B_{2g}$ transitions, respectively (Table 2). Therefore, it may be concluded that the complexes are distorted octahedral. The magnetic moment measurements in the range 1.7-1.8 B.M. are in close agreement with their electronic spectral data, which further supports their proposed structure.[26-29] Bands due to zeolite encapsulated Cu(II) complex appeared in the visible, and charge transfer bands appeared in the near-UV region; these values were very similar to the obtained values for the discrete neat complex.[26-29]

Several approaches have been used for the encapsulation of transition metal complexes in zeolite nanopores;[30] the choice of any specific method is dictated by the size of the ligand relative to the free diameter of the zeolite nanopores. Transition metal complexes or ligands that are smaller than the nanopores can be adsorbed from a solution phase into the
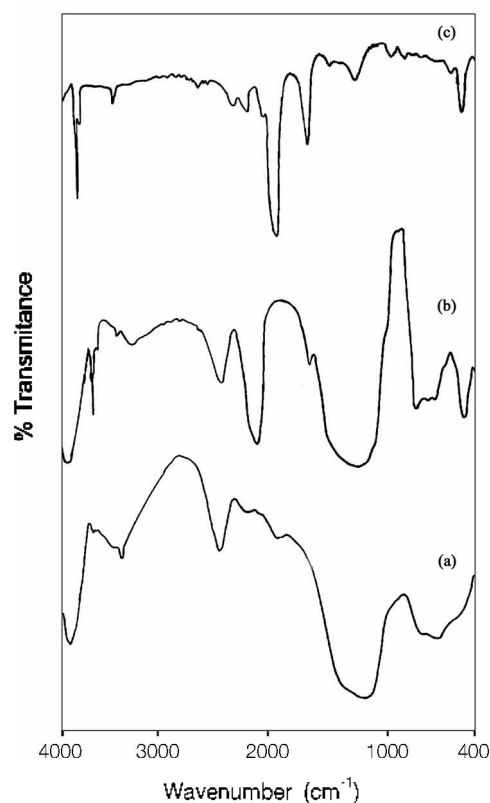
zeolite, or they can be synthesised via diffusion of the ligand into a metal-exchanged zeolite (Flexible Ligand Method, FLM). For complexes or ligands that are larger than the diameters of the channels, two approaches to prepare zeolites with encapsulated complexes have been developed. In one, the ligand is synthesized in situ in the presence of the transition metal ion, that can exist in the reaction media as a precursor complex, or that is exchanged into the zeolite. In the other, the pre-formed complexes are used as templates during zeolite synthesis (template synthesis method).

Encapsulation of the complexes was performed in the liquid phase by a two-step process that involves (i) adsorption of a copper(II) precursor complex; [bis(diamine)copper(II)] (diamine = 1,2-diaminoethane, 1,3-diaminopropane, 1,2-diaminobenzene, 1,3-diaminobenzene); $[Cu(N-N)_2]^{2+}$-NaY; and (ii) template condensation of the adsorbed copper complex with the thiodiglycolic acid. The resulting host guest nanocomposite materials; $[Cu([18]aneN_4S_2)]^{2+}$-NaY, $[Cu([20]$-aneN$_4$S$_2$)]$^{2+}$-NaY, $[Cu(Bzo_2[18]aneN_4S_2)]^{2+}$-NaY, $[Cu(Bzo_2$-[20]aneN$_4$S$_2$)$^{2+}$-NaY; were purified by Soxhlet extraction with different solvents. Soxhlet extraction was performed only for the zeolites with N$_4$S$_2$ complexes, the modified zeolites with $[Cu(N-N)_2]^{2+}$ were not purified by extraction as it was observed that this operation leads to a loss of the characteristic red color of the material. This observation provides an indication that $[Cu(N-N)_2]^{2+}$ is free to diffuse out of the zeolite. As these samples were not submitted to Soxhlet extraction, it was expected that they have copper complexes both inside the nanocavities and adsorbed onto the external surface. In order to characterise the resulting materials and to assess the efficiency of the encapsulation process, the parent zeolite and samples of host guest nanocomposite materials, were studied by several techniques and the obtained results compared.

The FLM (Scheme 2) lead to the encapsulation of Cu(II)

complexes of tetraoxo dithia tetraaza ligand inside the zeolite nanopore. According to elemental analysis (Table 3), the parent NaY zeolite has Si/Al molar ratio of 2.5 which corresponds to a unit cell formula $Na_{56}[(AlO_2)_{56}(SiO_2)_{136}]$. The unit cell formula of metal exchanged zeolites shows an initial metal loading in zeolite lattice is 3.86% $(Na_{34.4}Cu_{10.8}[(AlO_2)_{56}(SiO_2)_{136}]·nH_2O)$. The Si and Al contents in the metal-exchanged zeolites and the zeolite complexes are almost the same ratio as in the parent zeolite. This indicates little changes in the zeolite framework due to the absence of dealumination in metal ion exchange. The analytical data of each complex indicate Cu:C:N molar ratios almost close to those calculated for the mononuclear structure. Chemical composition confirmed the formation and purity of the complexes. It is estimated from the elemental analysis that the complex molecules occupy one in every four supercages of zeolite-Y. The elemental analysis results of the neat copper complexes showed near similarity to the theoretical values. The copper contents of the zeolite encapsulated complexes were estimated by dissolving known amounts of the obtained complexes in concentric HCl and using AAS. The analytical data of each neat complex indicate molar ratios of Cu:C:H almost close to those calculated for the mononuclear structure (Table 1). However, the presence of minute traces of free metal ions in the lattice could be assumed as the metal content which is slightly higher than the stoichiometric requirement. Only a portion of metal ions in metal-exchanged zeolite has undergone complexation and the rest is expected to be removed on re-exchange with sodium nitrate solution.

The X-ray powder diffractograms (XRD) of NaY, Cu(II)-NaY and $[Cu(N_4S_2)]^{2+}$-NaY were recorded to study their crystallinity and to ensure supporting. After careful comparison of XRD patterns of NaY and Cu(II)-NaY, it was observed that, there is one new peak with a d value of 1.8 nm in Cu(II)-NaY this peak was also observed in $[Cu(N_4S_2)]^{2+}$-NaY and [Cu-$(N_4S_2)](ClO_4)_2$ at the same position. In addition, the [Cu-
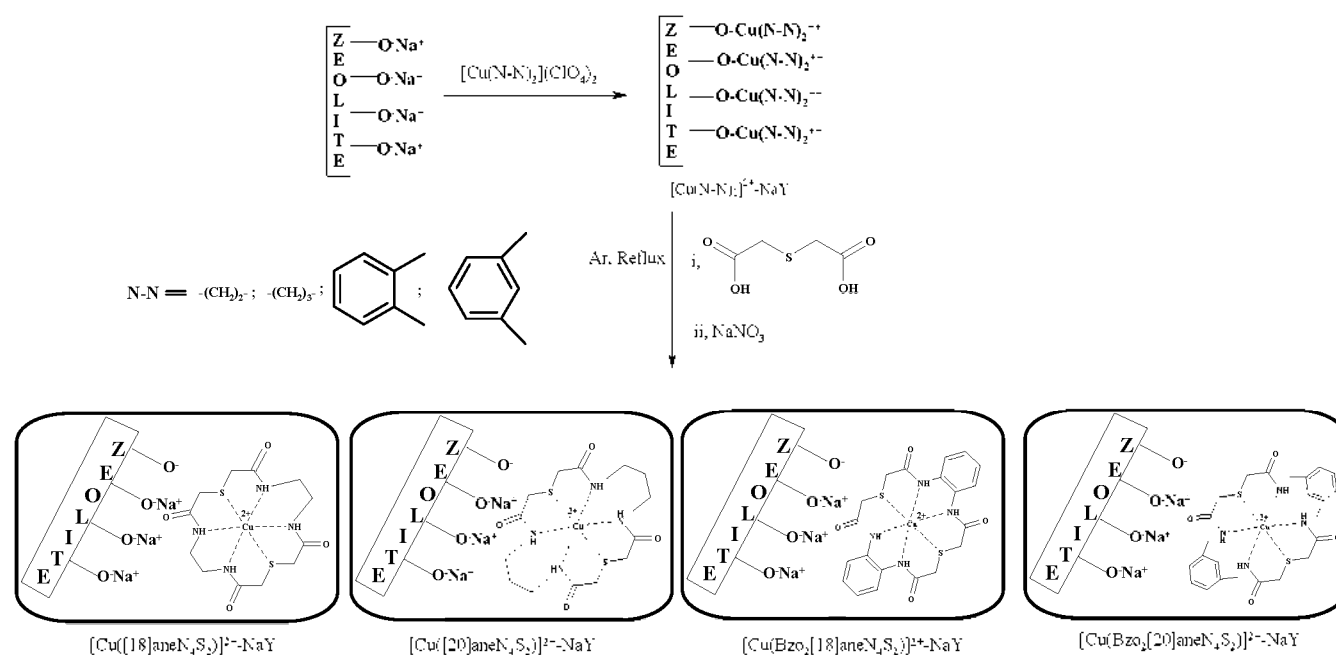
Scheme 2

$(N_4S_2)]^{2-}$-NaY exhibits one new signal with value of 8.3 nm, which is a part of the ligand as this signal was also observed in $[Cu(N_4S_2)](ClO_4)_2$ but not observed in NaY or Cu(II)-NaY. This information clearly indicates the support of $[Cu(N_4S_2)]^{2+}$ encapsulated in nanopores of zeolite. Very low intensity of other peaks made it difficult to distinguish them from the other peaks in the XRD pattern of the host guest nanocomposite materials. The SEM photographs of the samples taken before soxhlet extraction show the deposition of complexes on the external surface. However, the absence of extraneous materials in the SEM photographs of finished products indicates the complete removal of complexes surface which could be accomplished by extended extraction procedures.

IR spectroscopic data indicated that all of complexes encapsulated within nanocavity of zeolite (Fig. 1). The intensity of the peaks of nanocomposite material is, though, weak due to low concentration of the complex in zeolite, the IR spectrum of encapsulated complex is essentially similar to that of the free metal complex. No significant broadening or shift of the structure-sensitive zeolite vibrations at 1130 cm^{-1} (due to asymmetric T-O stretch) on encapsulation indicates that there is no significant expansion of the zeolite cavity or dealumination during the encapsulation process. This further indicates that structure of metal complex fit nicely within the nanocavity of the zeolite. The encapsulated complexes exhibit very similar IR data that are shifted 2-4 cm^{-1} relative to those of the corresponding free complexes (Table 3). These variations in band frequency can also be attributed to (i) distortions of the complexes, or to (ii) interactions with the zeolitic matrix (by electrostatic effects or coordination the higher negative charge of the zeolite host makes it a stronger ligand). Thus, IR and UV-Vis data indicates the encapsulation of tetraoxo dithia tetraaza macrocyclic complexes in the zeolite nanocavity.

The ^{1}H-NMR spectrum of all N_4S_2 macrocyclic ligands in $CDCl_3$ does not give any signal corresponding to primary amine and alcoholic protons. It shows a multiplet at ~8.6 ppm corresponding to amide CO-NH (4H) protons and does not show any signal corresponding to primary amine and alcoholic protons. A multiplet signal corresponding to methylene proton CO-N-CH$_2$ (8H) that are adjacent to the nitrogen atom appeared at ~3.4 ppm. NMR, spectrum also shows a singlet at ~2.4 ppm corresponding to CO-CH$_2$-S (8H) that is close to sulphor atom. For more investigation of structure, were synthesized the diamagnetic zinc(II) complexes. The ^{1}H-NMR spectrum of zinc complexes has been recorded in DMSO-d$_6$ as it is insoluble in CDCl$_3$. The ^{1}H-NMR spectra of all the zinc(II) complexes do not show any signal corresponding to primary amino and alcoholic protons. However, show multiplet in the region 8.5-8.7 ppm, which is assigned to amide (HN-CO, 4H) protons.[31] Another multiplet appeared in the region 3.4 ppm ($[Zn([18]aneN_4S_2)]^{2+}$) and 3.4 ppm ($[Zn([20]$-aneN$_4$S$_2$)]$^{2+}$), corresponding to the methylene protons[6] (CO-N-CH$_2$, 8H) which are adjacent to the nitrogen atoms. The multiplet appearing in the region δ 7.10-7.64 ppm has been assigned to phenyl protons ($[Zn(Bzo_2[18]aneN_4S_2)]^{2+}$ and $[Zn(Bzo_2[20]aneN_4S_2)]^{2+}$). Furthermore, a singlet in the region 2.44-2.5 ppm was observed assignable to methylene protons

Table 4. Surface area and pore volume data of host (nanopores of zeolite-Y) guest (N_4S_2 macrocyclic copper(II) complexes) nanocomposite materials.

Sample	Surface area[a] (m^2/g)	Pore volume[b] (ml/g)
NaY	545	0.3
Cu(II)-NaY	532	0.3
$[Cu([18]aneN_4S_2)]^{2-}$-NaY	387	0.2
$[Cu([20]aneN_4S_2)]^{2-}$-NaY	380	0.2
$[Cu(Bzo_2[18]aneN_4S_2)]^{2-}$-NaY	359	0.1
$[Cu(Bzo_2[20]aneN_4S_2)]^{2-}$-NaY	351	0.11

[a]Surface area is the "monolayer equivalent area" calculated as explained in the reference 21,22. [b]Calculated by the *t*-method.

(CO-CH$_2$-S, 8H) which are adjacent to the sulfur atom.

The nitrogen adsorption isotherms for the parent and the host-guest nanocomposite materials are typical of nanoporous solids; however, a decrease in the adsorption capacity of the zeolite was observed after adsorption of [bis(diamine)copper (II)] (diamine = 1,2-diaminoethane, 1,3-diaminopropane, 1,2-diaminobenzene, 1,3-diaminobenzene); $[Cu(N-N)_2]^{2-}$-NaY; and a further decrease after template condensation.

The pore volume and surface area have been calculated for encapsulated complexes (Table 4). The large reduction in surface area and in nanopore volume observed for the copper-based zeolites is interpreted as arising from the presence of compounds in the zeolite nanocavities. The values of the nanopore volume and surface area of host-guest nanocomposite materials: $[Cu([18]aneN_4S_2)]^{2-}$-NaY, $[Cu([20]aneN_4S_2)]^{2+}$-NaY, $[Cu(Bzo_2$-$[18]aneN_4S_2)]^{2+}$-NaY, $[Cu(Bzo_2[20]aneN_4S_2)]^{2-}$-NaY; are similar to those observed in NaY zeolites with entrapped porphyrinic, macrocyclic and azamacrocyclic complexes.[32] As the copper content in all samples is of the same magnitude, the observed lowering of the nanopore volume on going from [bis(diamine)-copper(II)] to $[Cu([18]aneN_4S_2)]^{2+}$, $[Cu([20]aneN_4S_2)]^{2-}$, $[Cu$-$(Bzo_2[18]aneN_4S_2)]^{2+}$ or $[Cu(Bzo_2[20]$ aneN$_4$S$_2$)$]^{2-}$- NaY must be attributed to the large volume of the latter complexes thus providing an additional confirmation that template condensation took place within the zeolite nanocavities.

The N_4S_2 macrocyclic copper(II) complexes undergo intense color changes due to deprotonation of the macrocyclic ligand in the presence of amine bases such as pyridine and Et$_3$N. Similar N-H deprotonations have been observed with other metal complexes containing N-H linkages. For the copper(II) complex, Et$_3$N is sufficiently basic to facilitate formation of the molecular complex. For preparation of the deprotonation form of $[Cu([18]aneN_4S_2)](ClO_4)_2$; Et$_3$N (0.5 cm^3) was added to a solution of 200 mg of $[Cu([18]aneN_4S_2)](ClO_4)_2$ in 15 cm^3 of MeCN. The deep-red product, which began precipitating within minutes, was filtered after 0.5 h under a N$_2$ atmosphere, washed with anhydrous ethanol, and dried in a vacuum. IR (KBr, cm^{-1}): 3140 (υ_{N-H}). $[Cu(C_{12}H_{18}O_4N_4S_2)]$ (I): Found: Cu, 15.2; C, 34.9; H, 4.2; N, 13.8. Calcd.: Cu, 15.5; C, 35.2; H, 4.4; N, 13.7%. The N-H stretching frequency of this compound $[Cu(C_{12}H_{18}O_4N_4S_2)]$, 3180 cm^{-1}, is reduced significantly from its dicationic precursor. $[Cu([18]aneN_4S_2)]$-$(ClO_4)_2$, 3270 cm^{-1}.
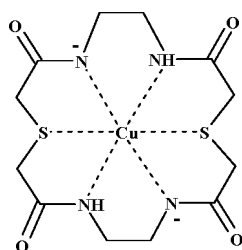
I

Conclusion

In summary, the results show that new octahedral dithia tetraaza: $[Cu([18]aneN_4S_2)]^{2-}$, $[Cu([20]aneN_4S_2)]^{2-}$, $[Cu(Bzo_2-[18]aneN_4S_2)]^{2+}$, $[Cu(Bzo_2[20]aneN_4S_2)]^{2-}$: can be encapsulated in the nanocavity of zeolite by template condensation between pre-entrapped: [bis(diamine) copper(II)] (diamine = 1,2-diaminoethane, 1,3-diaminopropane, 1,2-diaminobenzene, 1,3-diaminobenzene). $[Cu(N-N)_2]^{2-}$-NaY; complexes with thiodiglycolic acid. This strategy appears to be effective for the encapsulated of Cu(II) complexes with 18-, 20-membered tetraoxo dithia tetraaza macrocycle ligands derived from $[Cu(N-N)_2]^{2-}$-NaY. as template condensation in the nanocavity is still possible and no unreacted $[Cu(N-N)_2]^{2-}$ ions was detected. Furthermore, the spectroscopic data suggest that the encapsulated complexes experience very little distortion in the supercage and that the chemical ligation to the zeolite surface is minimal.

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