ORIGINAL ARTICLE

Host (nanopores of zeolite-Y)/guest (Ni(II)-tetraoxo dithia tetraaza macrocyclic complexes) nanocomposite materials: template synthesis and characterization

Masoud Salavati-Niasari

Abstract Nickel(II) complexes with six co-ordinate tetraoxo dithia tetraaza macrocyclic ligands derived from diamine and which provide a N_4S_2 co-ordination sphere, [18] aneN_4S_2: 1,4,10,13-tetraaza-5,9,14,18-tetraoxo-7,16-dithia-cyclooctadecane, [20]aneN_4S_2: 1,5,11,15-tetraaza-6,10,16,20-tetraoxo-8,18-dithia-cyclocosane, Bzo$_2$[18]aneN_4S_2: dibenzo-1,4,10,13-tetraaza-5,9,14,18-tetraoxo-7,16-dithia-cyclooctadecane, Bzo$_2$[20]aneN_4S_2: dibenzo-1,5,11,15-tetraaza-6,10,16,20-tetraoxo-8,18-dithia-cyclocosane, were entrapped in the nanopores of zeolite NaY by a two-step process in the liquid phase: (i) adsorption of [bis(diamine)-nickel(II)] (diamine = 1,2-diaminoethane, 1,3-diamino-propane, 1,2-diaminobenzene, 1,3-diaminobenzene); $[Ni(N–N)_2]^{2+}$-NaY; in the nanopores of the zeolite, and (ii) in situ template condensation of the nickel(II) precursor complex with thiodiglycolic acid. The mode of bonding and overall geometry of the complexes and new host/guest nanocomposite materials ($[Ni([18]aneN_4S_2)]^{2+}$-NaY, $[Ni([20]aneN_4S_2)]^{2+}$-NaY, $[Ni(Bzo_2[18]aneN_4S_2)]^{2+}$-NaY, $[Ni(Bzo_2[20]aneN_4S_2)^{2+}$-NaY) has been inferred through FT-IR, DRS and UV–vis spectroscopic techniques, molar conductance and magnetic moment data, XRD and elemental analysis, as well as nitrogen adsorption. An octahedral geometry around the nickel(II) ion is suggested for the complexes and new host/guest nanocomposite materials.

M. Salavati-Niasari
Institute of Nano Science and Nano Technology,
University of Kashan, Kashan 87317-51167, I.R. Iran

M. Salavati-Niasari (✉)
Department of Chemistry, Faculty of Science,
University of Kashan, Kashan 87317-51167, I.R. Iran
e-mail: salavati@kashanu.ac.ir

Introduction

Macrocyclic ligands are known to bind selectively metal ions, and are thus employed as carriers in metalselective extraction, phase transfer catalyses, membrane transport, and other related processes [1]. The stability of a macrocyclic metal complex depends upon a number of factors, including the number and type of the donor atoms present in the ligand and their relative positions within the macrocyclic skeleton, as well as the number and size of the chelate rings formed on complexation. For transition metal ions, features such as the nature and magnitude of crystal-field effects play also an important role [2].

Coordination geometry and properties of most transition metal complexes with macrocyclic mixed donor ligands containing mixed donors of nitrogen, oxygen and sulfur has been studied [3–16]. 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 nanporous materials have been used for those porous materials with pore diameters of <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].

Metal template condensation reaction provides selective routes toward products that are not obtainable in the absence of metal ions. Encapsulation of transition metal complexes in nanopores of zeolite and related materials is one of the subjects of current catalysis research due to their potentiality as biomimetic heterogeneous catalyst for the oxidation [18, 19]. In this paper, reported the synthesis and characterization of nickel(II) complexes of 18- and 20-membered dithia tetraoxo tetraaza macrocyclic ligands; [18]aneN$_4$S$_2$: 1,4,10, 13-tetraaza-5,9,14,18-tetraoxo-7,16-dithia-cyclooctadecane, [20]aneN$_4$S$_2$: 1,5,11,15-tetraaza-6,10,16,20-tetraoxo-8,18-dithia-cyclocosane, Bzo$_2$[18]aneN$_4$S$_2$: dibenzo-1,4,10,

13-tetraaza-5,9,14,18-tetraoxo-7,16-dithia-cyclooctadecane, Bzo$_2$[20]aneN$_4$S$_2$: dibenzo-1,5,11,15-tetraaza-6,10,16,20-tetraoxo-8,18-dithia-cyclocosane; encapsulated within the nanopores of zeolite-Y by the template condensation of thiodiglycolic acid and [bis(diamine)nickel(II)]; [Ni([18] aneN$_4$S$_2$)]$^{2+}$-NaY, [Ni([20]aneN$_4$S$_2$)]$^{2+}$-NaY; [Ni(Bzo$_2$[18] aneN$_4$S$_2$)]$^{2+}$-NaY; [Ni([20]aneN$_4$S$_2$)]$^{2+}$-NaY; shown in Schemes 1, 2.

Experimental

*Safety note-*Nickel perchlorate salt with organic ligands is often explosive and should be handled with caution. All 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,

Scheme 1

[Ni([18]aneN$_4$S$_2$)]$^{2+}$-NaY
[Ni([20]aneN$_4$S$_2$)]$^{2+}$-NaY
[Ni(Bzo$_2$[18]aneN$_4$S$_2$)]$^{2+}$-NaY
[Ni(Bzo$_2$[20]aneN$_4$S$_2$)]$^{2+}$-NaY

[Ni(N-N)$_2$]$^{2+}$-NaY
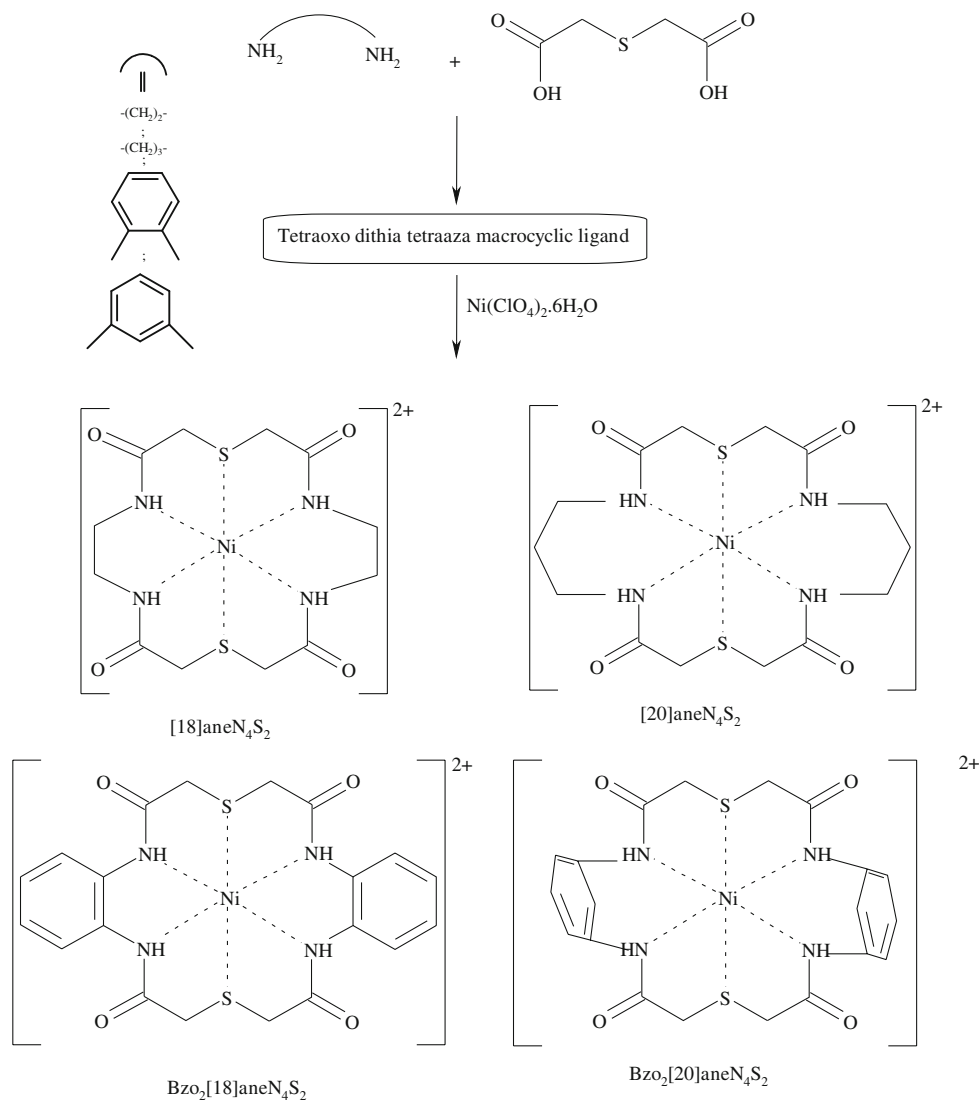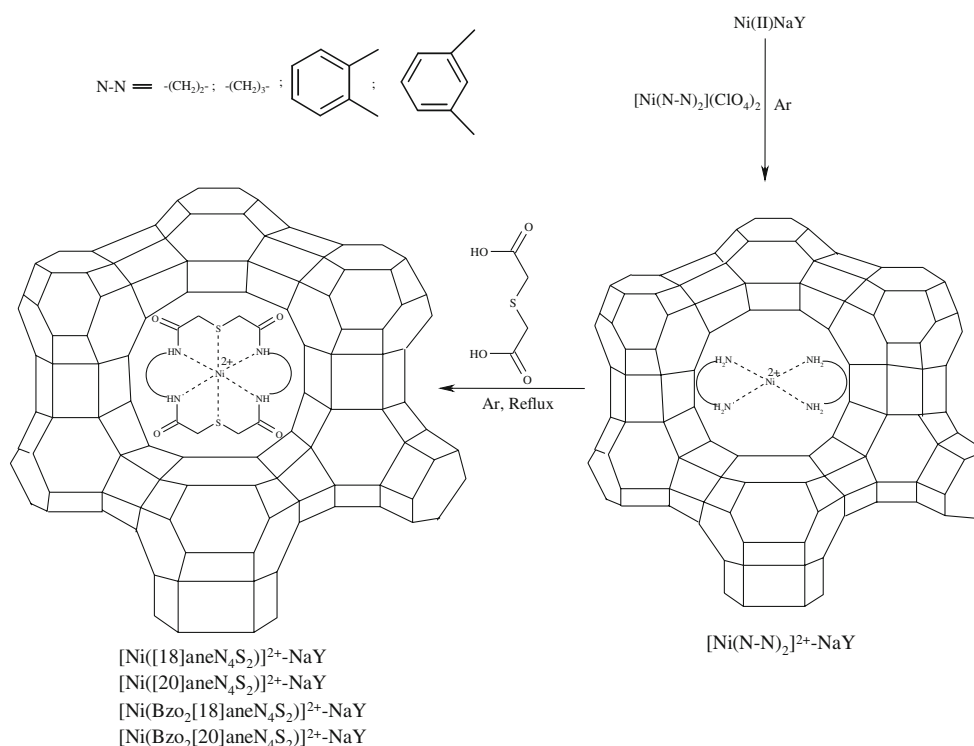
Scheme 2

1,2-diaminobenzene, 1,3-diaminobenzene was obtained from Merck. Solvents were dried before used. The complex [Ni(N–N)$_2$](ClO$_4$)$_2$ was prepared according to the published procedures [20]. 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$_\alpha$ radiation. 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. 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. The amounts of metallocomplexes encapsulated in zeolite matrix were determined by the elemental analysis and followed by subtracting the amount of metallocomplex left from the solutions after the synthesis of the catalysts as determined by UV–vis spectroscopy, from the amount taken for the synthesis. 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.

Synthesis of tetraoxo dithia tetraaza macrocyclic ligand

Tetraoxo dithia tetraaza macrocyclic ligands ([18]aneN$_4$S$_2$, [20]aneN$_4$S$_2$, Bzo$_2$[18]aneN$_4$S$_2$ or Bzo$_2$[20]aneN$_4$S$_2$) were prepared by following the procedures reported in Ref. [23]. The ligand has been synthesized by the condensation reaction of the thioglycolic 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 hydrochloric acid (~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 [Ni([18 or 20]aneN$_4$S$_2$)](ClO$_4$)$_2$ and [Ni(Bzo$_2$[18 or 20]aneN$_4$S$_2$)](ClO$_4$)$_2$ complexes

Nickel(II) perchlorate hexahydrate (3.66 g, 0.01 mol) dissolved in ethanol (20 ml) was reacted with an ethanolic (20 mL) solution of tetraoxo dithia tetraaza ligands ([18]aneN$_4$S$_2$, [20]aneN$_4$S$_2$, Bzo$_2$[18]aneN$_4$S$_2$ or Bzo$_2$[20] aneN$_4$S$_2$) (0.01 mol) by refluxing for 1 h under nitrogen atmosphere. The mixture was heated at reflux for 6 h until an orange solution resulted. The solution was cooled to room temperature and filtered to remove nickel 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 [Ni(N–N)$_2$]$^{2+}$-NaY

Typically a 4 g sample of NaY zeolite was mixed with 0.37 g of [bis(diamine)nickel(II)] perchlorate; diamine = 1,2-diaminopropane, 1,3-diaminopropane, 1,2-diaminobenzene or 1,3-diaminobenzene; suspended in 100 mL of methanol and then refluxed for 8 h. The pale yellow solid consisting of [Ni(N–N)$_2$]$^{2+}$ exchanged with Na$^+$ in NaY and denoted as [Ni(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 Ni(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.

Preparation of [Ni([18 or 20]aneN$_4$S$_2$)]$^{2+}$-NaY and [Ni(Bzo$_2$[18 or 20]aneN$_4$S$_2$)]$^{2+}$-NaY

To a stirred methanol suspension (100 mL) of [Ni(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 pale yellow 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 amine-ester condensation and any nickel(II) complexes adsorbed onto the external surface of the zeolite crystallines. The resulting pale pink solids were dried at 70 °C under vacuum for 12 h. The remaining [bis(diamine)nickel(II)] ions in zeolite were removed by exchanging with aqueous 0.1 M NaNO$_3$ 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

Nickel(II) reacted with 18- and 20-membered tetraoxo dithia tetraaza macrocyclic ligands ([18]aneN$_4$S$_2$, [20]aneN$_4$S$_2$, Bzo$_2$[18]aneN$_4$S$_2$ and Bzo$_2$[20]aneN$_4$S$_2$) in presence of LiClO$_4$ to yield the cationic complexes; [Ni([18]aneN$_4$S$_2$)](ClO$_4$)$_2$, [Ni([20]aneN$_4$S$_2$)](ClO$_4$)$_2$, [Ni(Bzo$_2$[18]aneN$_4$S$_2$)](ClO$_4$)$_2$ and [Ni(Bzo$_2$[20]aneN$_4$S$_2$](ClO$_4$)$_2$; (Scheme 1).

The ^{1}H-NMR a spectrum of all tetraoxo dithia tetraaza macrocyclic ligands in CDCl$_3$ does not give any signal corresponding to primary amine and alcoholic protons. It shows a multiplet at $\sim$8.60 ppm corresponding to amide CO-NH (4H) protons and does not show any signal corresponding to primary amine and alcoholic protons. A multiplet signal corresponding to methylene proton CO–N–CH$_2$ (8H) that are adjacent to the nitrogen atom appeared at $\sim$3.40 ppm. NMR spectrum also shows a singlet at $\sim$2.35 ppm corresponding to CO–CH$_2$–S (8H) that is close to sulfur atom.

The infrared spectra of the complexes (Table 1) do 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 1630–1636, 1528–1534, 1250–1253 and 650–654 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 [ϕ(C=O)] bands, respectively, which support the macrocyclic structure. A single sharp band observed in the region 3220–3230 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 $\sim$450 cm^{-1} attributable to υ(M–N) which provide strong evidence for the involvement of nitrogen in coordination [25]. The results of elemental analysis (Table 1) support the proposed macrocyclic structure.

The proposed molecular formula of a macrocyclic Ni(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+}): 506, 407 ([Ni([18]aneN$_4$S$_2$)](ClO$_4$)$_2$); 534, 435 [Ni([20]aneN$_4$S$_2$)](ClO$_4$)$_2$; 602, 503 [Ni(Bzo$_2$[18]aneN$_4$S$_2$)](ClO$_4$)$_2$; 602, 503 [Ni(Bzo$_2$[20]aneN$_4$S$_2$](ClO$_4$)$_2$. This data is in good agreement with the respective molecular formulae. 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).

DMSO solutions of these complexes were conductive (Table 2). Unfortunately, I could not grow any single

Table 1 Elemental analysis, vibrations parameters and molecular ion peaks for ligands and tetraoxo dithia tetraaza macrocyclic nickel(II) complexes

Complex	Calculated (found)					IR (KBr, cm^{-1})						FAB mass (m/z)	
	C (%)	H (%)	N (%)	C/N	M (%)	I	II	III	IV	υ_{N-H}	υ_{M-N}	[M-ClO$_4$]$^+$	[M-2ClO$_4$]$^{2+}$
[18]aneN$_4$S$_2$	41.37 (41.13)	5.79 (5.60)	16.08 (16.20)	2.57 (2.54)	–	1645	1572	1246	662	3205	–	–	–
[Ni([18]aneN$_4$S$_2$)](ClO$_4$)$_2$	23.78 (23.52)	3.33 (3.20)	9.24 (9.35)	2.57 (2.52)	9.69 (9.50)	1632	1530	1250	652	3223	450	506	407
[20]aneN$_4$S$_2$	44.66 (44.42)	6.43 (6.25)	14.88 (14.96)	3.00 (2.97)	–	1641	1570	1244	662	3200	–	–	–
[Ni([20]aneN$_4$S$_2$)](ClO$_4$)$_2$	26.52 (26.30)	3.81 (3.63)	8.84 (8.96)	3.00 (2.94)	9.26 (9.13)	1630	1528	1251	650	3220	447	534	435
Bzo$_2$[18]aneN$_4$S$_2$	54.04 (53.88)	4.53 (4.37)	12.60 (12.75)	4.29 (4.23)	–	1650	1571	1248	661	3286	–	–	–
[Ni(Bzo$_2$[18]aneN$_4$S$_2$)](ClO$_4$)$_2$	34.21 (34.02)	2.87 (2.70)	7.98 (8.11)	4.29 (4.19)	8.36 (8.18)	1636	1534	1253	654	3230	456	602	503
Bzo$_2$[20]aneN$_4$S$_2$	54.04 (53.86)	4.53 (4.40)	12.60 (12.72)	4.29 (4.23)	–	1648	1571	1248	662	3284	–	–	–
[Ni(Bzo$_2$[20]aneN$_4$S$_2$)](ClO$_4$)$_2$	34.21 (34.00)	2.87 (2.73)	7.98 (8.13)	4.29 (4.18)	8.36 (8.20)	1635	1532	1252	652	3228	453	602	503

crystals suitable for X-ray crystallographic studies. The molar conductance values (106–130 Ω^{-1} mol^{-1} cm^2) and measured of tetraoxo dithia tetraaza 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 Ni(II) tetraoxo dithia tetraaza macrocycle complexes indicated that the tetraoxo dithia tetraaza ligands of this study do not differ significantly from the dithia tetraaza ligands respect to the ligand field strength.

The electronic spectra of all nickel complexes show two distinct bands at 12,106–13,070 and 17,250–17,450 cm^{-1} which are assigned as $3A_{2\,g}(F) \rightarrow 3T_{1\,g}(F)$ and $3A_{2\,g}(F) \rightarrow 3T_{1\,g}(P)$ transitions, respectively, suggesting an octahedral environment around the nickel ions [26]. The observed magnetic moment values in the range 2.95–3.11 BM is consistent with the above geometry [27]. Comparing the obtained magnetic measurement at room temperature and the results of electronic spectra (Table 2) of metal complexes with octahedral Ni(II) macrocycle complexes indicated that the N$_4$S$_2$ ligands of this study do not differ significantly from the dithia tetraaza ligands respect to the ligand field strength.

The 18- and 20-membered tetraoxo dithia tetraaza macrocyclic nickel(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 nickel(II) complex, Et$_3$N is sufficiently basic to facilitate formation of the molecular complex. For preparation of the deprotonation form of [Ni([18]aneN$_4$S$_2$)](ClO$_4$)$_2$; Et$_3$ N (0.5 mL) was added to a solution of 200 mg of [Ni([18]aneN$_4$S$_2$)](ClO$_4$)$_2$ in 15 mL of CH$_3$CN. The deep-yellow product, which began precipitating within minutes, was filtered after 0.5 h under a N$_2$ atmosphere, washed with anhydrous EtOH, and dried in a vacuum. The product characterized by elemental analysis and IR spectroscopy. The elemental analysis data presented [Ni(C$_{12}$H$_{18}$O$_4$N$_4$S$_2$)] (I) formula.

(I)
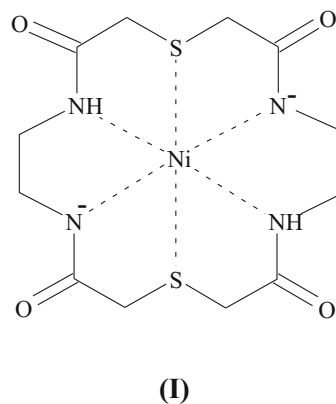
Table 2 Magnetic moment, electronic spectral and molar conductance values of the tetraoxo dithia tetraaza macrocyclic nickel(II) complexes

Sample	$3A_{2g}$ (F) → $3T_{1g}$(F) cm^{-1}, (ε, dm^3 mol^{-1} cm^{-1})	$3A_{2g}$ (F) → $3T_{1g}$ (P) cm^{-1}, (ε, dm^3 mol^{-1} cm^{-1})	μ_{eff} (Mb)	$\Lambda_M{}^a$, Ω^{-1} cm^2 M^{-1}
[Ni([18]aneN$_4$S$_2$)](ClO$_4$)$_2$	12,200 (17)	17,300 (26)	3.11	130
[Ni([20]aneN$_4$S$_2$)](ClO$_4$)$_2$	12,106 (20)	17,250 (30)	3.08	125
[Ni(Bzo$_2$[18]aneN$_4$S$_2$)](ClO$_4$)$_2$	13,070 (16)	17,450 (22)	2.98	115
[Ni(Bzo$_2$[20]aneN$_4$S$_2$)](ClO$_4$)$_2$	13,040 (18)	17,410 (24)	2.95	106

^{a} In DMSO solutions

The N–H stretching frequency of this compound [Ni(C$_{12}$H$_{18}$O$_4$N$_4$S$_2$)], 3140 cm^{-1}, is reduced significantly from its dicationic precursor, [Ni([18]aneN$_4$S$_2$)](ClO$_4$)$_2$, 3223 cm^{-1}.

Encapsulation of the complexes was performed in the liquid phase by a two-step process that involves (i) adsorption of a nickel(II) precursor complex; [bis(diamine) nickel(II)] (diamine = 1,2-diaminoethane, 1,3-diamino-propane, 1,2-diaminobenzene, 1,3-diaminobenzene); [Ni(N–N)$_2$]$^{2+}$-NaY; and (ii) in situ template condensation of the adsorbed nickel complex with the thiodiglycolic acid. The resulting host guest nanocomposite materials; [Ni([18]aneN$_4$S$_2$)]$^{2+}$-NaY, [Ni([20]aneN$_4$S$_2$)]$^{2+}$-NaY, [Ni (Bzo$_2$[18]aneN$_4$S$_2$)]$^{2+}$-NaY, [Ni(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 the tetraoxo dithia tetraaza complexes, the modified zeolites with [Ni(N–N)$_2$]$^{2+}$ were not purified by extraction as it was observed that this operation leads to a loss of the characteristic yellow color of the material. This observation provides an indication that [Ni(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 nickel complexes both inside the nanocavities and adsorbed onto the external surface. In order to characterize 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 flexible ligand synthesis (Scheme 2) leads to the encapsulation of Ni(II) complexes of tetraoxo dithia tetraaza macrocyclic ligands ([18]aneN$_4$S$_2$, [20]aneN$_4$S$_2$, Bzo$_2$[18]aneN$_4$S$_2$ and Bzo$_2$[20]aneN$_4$S$_2$) inside the nanopores of zeolite. The results of chemical analysis of the samples are given in Table 3. 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 11.1 moles of nickel dispersion per unit cell (Na$_{34}$Ni$_{11.1}$[(AlO$_2$)$_{56}$(SiO$_2$)$_{136}$] · nH$_2$O). Metal ion exchange at around 34% leads to 2.70–3.70% of metal loading in zeolite.

The CHN analysis results of the neat nickel complexes showed near similarity to the theoretical values. The nickel contents of the zeolite encapsulated catalysts 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 Ni: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 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 X-ray diffraction patterns of zeolite-containing azamacrocyclic complexes are similar to those of metal-exchanged zeolites and the parent NaY zeolite. The zeolite crystallinity is retained on encapsulating

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

Sample	C (%)	H (%)	N (%)	C/N	Si (%)	Al (%)	Na (%)	Ni (%)	Si/Al	I	II	III	d↔d (cm^{-1})
NaY	–	–	–	–	21.76	8.60	7.50	–	2.53	–		–	–
Ni(II)-NaY	–	–	–	–						–		–	–
[Ni([18]aneN$_4$S$_2$)]$^{2+}$-NaY	4.17	1.76	1.79	2.33	21.16	8.36	5.40	2.76	2.53	1636	1534	3220	12,240, 17,320
[Ni([20]aneN$_4$S$_2$)]$^{2+}$-NaY	4.23	1.80	1.58	2.67	21.13	8.35	5.38	2.74	2.53	1633	1530	3218	12,200, 17,280
[Ni(Bzo$_2$[18]aneN$_4$S$_2$)]$^{2+}$-NaY	4.45	1.85	1.13	3.94	21.03	8.31	5.31	2.68	2.53	1640	1538	3227	13,090, 17,500
[Ni(Bzo$_2$[20]aneN$_4$S$_2$)]$^{2+}$-NaY	4.48	1.89	1.13	3.97	21.06	8.32	5.33	2.65	2.53	1638	1335	3223	13,060, 17,430

azamacroclic complexes. The crystalline phases of free metal ions or the encapsulated azamacrocyclic complexes were not detected in any of the patterns because of rendering their fine dispersion in zeolite which non-detectable by XRD. 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. The intensity of the peaks of encapsulated complex 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 fitted nicely within the nanocavity of the zeolite. The entrapped complexes exhibit very similar IR data that are shifted 2–4 cm^{-1} relative to those of the corresponding free complexes (Table 1). 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 co-ordination- the higher negative charge of the zeolite host makes it a stronger ligand). Bands due to zeolite encapsulated Ni(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, 27]. Thus, IR and UV–vis data indicates the encapsulation of tetraoxo dithia tetraaza macrocyclic complexes in the zeolite nanocavity.

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)nickel(II)] (diamine = 1,2-diaminoethane, 1, 3-diaminopropane, 1,2-diaminobenzene, 1,3-diaminobenzene); [Ni(N–N)$_2$]$^{2+}$-NaY;, and a further decrease after template condensation. The pore volume and surface area have been calculated and are presented in Table 4. The large reduction in surface area and in nanopore volume observed for the nickel-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; [Ni([18]aneN$_4$S$_2$)]$^{2+}$-NaY, [Ni([20]aneN$_4$S$_2$)]$^{2+}$-NaY, [Ni(Bzo$_2$[18]aneN$_4$S$_2$)]$^{2+}$-NaY, [Ni(Bzo$_2$[20]aneN$_4$S$_2$)$^{2+}$-NaY; are similar to those observed in NaY zeolites with

Table 4 Surface area and pore volume data of host (nanopores of zeolite-Y) guest (tetraoxo dithia tetraaza macrocyclic nickel(II) complexes) nanocomposite materials

Sample	Surface area[a] (m^2/g)	Pore volume[b] (ml/g)
NaY	545	0.31
Ni(II)-NaY	528	0.31
[Ni([18]aneN$_4$S$_2$)]$^{2+}$-NaY	398	0.19
[Ni([20]aneN$_4$S$_2$)]$^{2+}$-NaY	391	0.18
[Ni(Bzo$_2$[18]aneN$_4$S$_2$)]$^{2+}$-NaY	370	0.15
[Ni(Bzo$_2$[20]aneN$_4$S$_2$)]$^{2+}$-NaY	358	0.13

[a] Surface area is the "monolayer equivalent area" calculated as explained in the Ref. [21, 22]

[b] Calculated by the t-method

entrapped porphyrinic, macrocyclic and azamacrocyclic complexes [28]. As the copper content in all samples is of the same magnitude, the observed lowering of the nanopore volume on going from [bis(diamine)nickel(II)] to [Ni ([18]aneN$_4$S$_2$)]$^{2+}$, [Ni([20]aneN$_4$S$_2$)]$^{2+}$, [Ni(Bzo$_2$[18]ane N$_4$S$_2$)]$^{2+}$ or [Ni(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 powder X-ray diffraction patterns of NaY, Ni(II)-NaY and [Ni(N$_4$S$_2$)]$^{2+}$-NaY were recorded at 2θ values between 5° and 70°. The diffraction patterns of encapsulated metal complexes, NaY, Ni(II)-NaY are essentially similar except a slight change in the intensity of the bands in encapsulated complexes. These observations indicate that the framework of the zeolite has not undergone any significant structural change during encapsulation. This is expected as ligand being flexible in nature enters slowly through pores of the zeolite and fits nicely in the cavity upon coordination with the metal ions. One new but week peaks due to neat complexes were detected in the encapsulated zeolite at 2θ values of 8.29 due to loading of metal complexes.

Conclusion

The new octahedral tetraoxo dithia tetraaza; [Ni([18]ane N$_4$S$_2$)]$^{2+}$, [Ni([20]aneN$_4$S$_2$)]$^{2+}$, [Ni(Bzo$_2$[18]aneN$_4$S$_2$)]$^{2+}$, [Ni(Bzo$_2$[20]aneN$_4$S$_2$)$^{2+}$; have been encapsulated in the nanocavity of zeolite by template condensation between pre-entrapped; [bis(diamine)nickel(II)] (diamine = 1,2-di-aminoethane, 1,3-diaminopropane, 1,2-diaminobenzene, 1,3-diaminobenzene), [Ni(N–N)$_2$]$^{2+}$-NaY; complexes with thiodiglycolic acid. This strategy appears to be effective for the encapsulated of Ni(II) complexes with 18-, 20-membered tetraoxo dithia tetraaza macrocycle ligands derived from [Ni(N–N)$_2$]$^{2+}$-NaY, as template condensation in the

nanocavity is still possible and no unreacted [Ni(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.

References

1. Kumar, D.S., Alexander, V.: Macrocyclic complexes of lanthanides in identical ligand frameworks part 1. Synthesis of lanthanide(III) and yttrium(III) complexes of an 18-membered dioxatetraaza macrocycle. Inorg. Chim. Acta **238**, 63–71 (1995); Alexander, V.: Design and synthesis of macrocyclic ligands and their complexes of lanthanides and actinides. Chem. Rev. **95**, 273–342 (1995)
2. Lindoy, L.F.: The Chemistry of Macrocyclic Ligand Complexes. Cambridge University Press, Cambridge (1989)
3. Salavati-Niasari, M., Najafian, H.: One-pot template synthesis and properties of Ni(II) complexes of 16-membered hexaaza macrocycles. Polyhedron **22**, 2633–2638 (2003); Salavati-Niasari, M., Rezai-Adaryani, M.: Template condensation reactions of formaldehyde with amines and 2,3-butanedihydrazone: preparation and properties of nickel(II) complexes of 18-membered decaaza macrocycles. Polyhedron **23**, 1325–1331 (2004); Salavati-Niasari, M.: Macrocyclic dioxadiaza from the reaction of the (1,8-diamino-3,6-dioxaoctane)copper(II) cation with formaldehyde and the carbon acids nitroethane or diethylmalonate. Polyhedron **24**, 1405–1409 (2005); Salavati-Niasari, M.: Zeolite-encapsulation copper(II) complexes with 14-membered hexaaza macrocycles: synthesis, characterization and catalytic activity. J. Mol. Catal. A: Chem. **217**, 87–92 (2004)
4. Chaudhuri, P., Wieghardt, K.: The chemistry of 1,4,7-triazacyclononane and related tridentate macrocyclic compounds. Prog. Inorg. Chem. **35**, 329–436 (1987)
5. Bhula, R., Osvath, P., Weatherburn, D.C.: Complexes of tridentate and pentadentate macrocyclic ligands. Coord. Chem. Rev. **91** 89–213 (1988); Hay, R.W., Dandy, A., Lightfoot, P., Lampeka, Y.D.: Padlock macrocyclic complexes. The synthesis of a range of nickel(II) complexes of N-alkyl azacyclams and the crystal structure of (3-ethyl-1,3,5,8,12-penta-azacyclotetradecane) nickel(II) perchlorate. Polyhedron **16**, 2777–2783 (1997); Hay, R.W., Cromie, T.J., Lightfoot, P.: The synthesis and crystal structure of [NiL(NCS)2] (L = 3-hydroxyethyl-1,3,5,8,12-pentaazacyclotetradecane). Trans. Metal Chem. **22**, 510–512 (1997)
6. Casabo, J., Escriche, L., Alegret, S., Jaime, C., Jimenez, C.P., Mestres, L., Rius, J., Molind, E., Miravitlles, C., Teixidor, F.: Pyridine-based macrocycles containing N, O, and S and their use as ion-selective electrodes. Crystal structures of 15-aza-6-oxa-3,9-dithiabicyclo[9.3.1]pentadeca-1(15),11,13-triene and (15-aza-6-oxa-3,9-dithiabicyclo[9.3.1]pentadeca-1(15),11,13-triene)dichlorocopper(II). Inorg. Chem. **30**, 1893–1898 (1991)
7. Suh, M.P., Oh, K.Y., Lee, J.W., Boe, Y.Y.: Acetamide coordination in a nickel(I) macrocyclic complex: synthesis, properties, and X-ray crystal structure of a five-coordinate nickel(I) iminol complex of 1,3,6,8,12,15-hexaazatricyclo[13.3.1.1^{8,12}] icosane. J. Am. Chem. Soc. **118**, 777–783 (1996)
8. Fabrizzi, L., Kaden, T.A., Perotti, A., Seghi, B., Siegfried, L.: Complexation of divalent and trivalent nickel and copper ions by rigid and flexible dioxo tetraaza macrocycles. Inorg. Chem. **25**, 321–327 (1986)
9. Woollins, J.D., Kelly, P.F.: The preparation and properties of compounds containing Pt(III). Coord. Chem. Rev. **65**, 115–140 (1985)
10. Comba, P., Curtis, N.F., Lawrence, G.A., O'Leary, M.A., Skelton, B.W., White, A.H.: Comparisons of thirteen- to sixteen-membered tetra-azacycloalkane copper(II) complexes derived from template syntheses involving nitroethane and formaldehyde. Crystal structures of (10-methyl-10-nitro-1,4,8,12-tetra-azacyclopentadecane)copper(II) and (3-methyl-3-nitro-1,5,9,13-tetra-azacyclohexadecane)copper(II) perchlorates. J. Chem. Soc., Dalton Trans. 2145–2152 (1988)
11. Wainwright, K.P.: Synthetic and structural aspects of the chemistry of saturated polyaza macrocyclic ligands bearing pendant coordinating groups attached to nitrogen. Coord. Chem. Rev. **166**, 35–90 (1997)
12. Lawrence, G.A., O'Leary, M.A.: Macrocyclic tetraamines from reaction of the (1,10-diamino-4,7-diazadecane)copper(II) cation with formaldehyde and the carbon acids nitroethane and diethylmalonate: variability in reactivity. Polyherdon **6**, 1291–1294 (1987)
13. Suh, M.P., Shin, W., Kim, D., Kim, S.: Preparation and molecular structure of the nickel(II) perchlorate complex of a hexadentate macrobicyclic ligand, 1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6] eicosane. Inorg. Chem. **23**, 618–620 (1984)
14. Salavati-Niasari, M.: Oxidation of tetrahydrofuran with hydrogen peroxide in the presence of host (zeolite Y)/guest (1,9-dialkyl-1,3,7,9,11,15-hexaazacyclohexadecane copper(II) complexes, [Cu(R$_2$[16]aneN$_6$)]$^{2+}$) nanocomposite materials. Inorg. Chem. Commun. **9**, 628–633 (2006); Salavati-Niasari, M., Davar, F.: Host (nanodimensional pores of zeolite Y)–guest (3,10-dialkyl-dibenzo-1,3,5,8,10,12-hexaazacyclotetradecane, [Ni(R$_2$Bzo$_2$[14] aneN$_6$)]$^{2+}$) nanocomposite materials: synthesis, characterization and catalytic oxidation of cyclohexene. Inorg. Chem. Commun. **9**, 263–268 (2006); Salavati-Niasari, M., Davar, F.: Synthesis, characterization and catalytic activity of copper(II) complexes of 14-membered macrocyclic ligand; 3,10-dialkyl-dibenzo-1,3,5,8,10,12-hexaazacyclotetradecanel/zeolite encapsulated nanocomposite materials. Inorg. Chem. Commun. **9**, 304–309 (2006); Salavati-Niasari, M.: Host (nanocavity of zeolite-Y)–guest (tetraaza[14]annulene copper(II) complexes) nanocomposite materials: synthesis, characterization and liquid phase oxidation of benzyl alcohol. J. Mol. Catal. A: Chem. **245**, 192–199 (2006); Salavayi-Niasari, M.: Synthesis and characterization of host (nanodimensional pores of zeolite-Y)–guest [Unsaturated 16-membered octaaza-macrocycle manganese(II), cobalt(II), nickel(II), copper(II), and zinc(II) complexes] nanocomposite materials. Chem. Lett. **34**, 1444–1445 (2005)
15. Curtis, N.F.: Macrocyclic coordination compounds formed by condensation of metal-amine complexes with aliphatic carbonyl compounds. Coord. Chem. Rev. **3**, 3–47 (1968)
16. Shakir, M., Varkey, S.P., Nasman, O.S.M.: Transition metal complexes of 20–22-membered octaazamacrocycles: synthesis and characterization. Polyhedron **14**, 1283–1288 (1995); Shakir, M., Varkey, S.P.: A new synthetic route for the preparation of a new series of 14–22-membered tetraoxomacrocyclic tetraamines and their transition metal complexes. Polyhedron **14**, 1117–1127 (1995)
17. Schüth, F., Schmidt, W.: Microporous and mesoporous materials. Adv. Mater. **14** 629–638 (2002); Schuth, F., Sing, K., Weitkamp, J. (eds.): Handbook of Porous Solids, Vol. I–V. Wiley-VCH, Weinheim (2002) and references therein
18. Vankelecom, I.F.J., Parton, R.F., Casselman, M.J.A., Uytterhoeven, J.B., Jacobs, P.A.: Oxidation of cyclohexane using FePcY-Zeozymes occluded in polydimethylsiloxane membranes. J. Catal. **163**, 457–464 (1996); Knops-Gerrits, P.P., De Vos, D.E., Jacobs, P.A.: Oxidation catalysis with semi-inorganic zeolite-based Mn

catalysts. J. Mol. Catal. A: **117**, 57–70 (1997); Maurya, M.R., Titinchi, S.J.J., Chand, S.: Catalytic activity of chromium(III), iron(III) and bismuth(III) complexes of 1,2-bis(2-hydroxyben-zamido)ethane (H$_2$hybe) encapsulated in zeolite-Y for liquid phase hydroxylation of phenol. J. Mol. Catal. A: Chem. **214**, 257–264 (2004); Raja, R., Ratnaswamy, P.: Oxyhalogenation of aromatics over copper phthalocyanines encapsulated in zeolites. J. Catal. **170**, 244–253 (1997); Kantam, M.L., Ranganath, K.V.S., Sateesh, M., Kumar, K.B.S., Manoranjan, B.: Friedel–Crafts acylation of aromatics and heteroaromatics by beta zeolite. J. Mol. Catal. A: Chem. **225**, 15–20 (2005); Hardacre, C., Katdare, S.P., Milroy, D., Nancarrow, P., Rooney, D.W., Thompson, J.M.: A catalytic and mechanistic study of the Friedel–Crafts benzoylation of anisole using zeolites in ionic liquids. J. Catal. **227**, 44–52 (2004); Choudhary, V.R., Jana, S.K., Patil, N.S., Bhargava, S.K.: Friedel–Crafts type benzylation and benzoylation of aromatic compounds over Hβ zeolite modified by oxides or chlorides of gallium and indium. Microporous Mesoporous Mater. **57**, 21–35 (2003)

19. Hartman, M.: Selective oxidations of linear alkanes with molecular oxygen on molecular sieve catalysts-A breakthrough? Angew. Chem. Int. Ed. **39**, 888–890 (2000); Salavati-Niasari, M.: Nanoscale microreactor-encapsulation 14-membered nickel(II) hexamethyl tetraaza: synthesis, characterization and catalytic activity. J. Mol. Catal. A: Chem. **229**, 159–164 (2005); Salavati-Niasari, M.: Nanoscale microreactor-encapsulation of 18-membered decaaza macrocycle nickel(II) complexes. Inorg. Chem. Commun. **8**, 174–177 (2005); Salavati-Niasari, M.: Zeolite-encapsulated nickel (II) complexes with 14-membered hexaaza macrocycle: synthesis and characterization. Inorg. Chem. Commun. **7**, 963–966 (2004)

20. Basset, J., Denney, G.H., Jeffery, G.H., Mendham, J.: Vogel's Textbook of Quantitative Inorganic Analysis, p. 429. Wiley, New York (1987)

21. Sing, S.W., Everett, H., Haul, R.A.W., Moscou, L., Pierotti, R.A., Rouquerol, J., Siemieniewska, T.: Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity. Pure Appl. Chem. **57**, 603–605 (1985)

22. Lineares-Solano, A.: Textural characterization of porous carbons by physical adsorption of gases. In: Figueiredo, J.L., Moulijn, J.A. (eds.) Carbon and Coal Gasifcation, p. 137. Martinus Nijho, Dordrecht, MA (1986)

23. Chandra, S., Gupta, L.K.: Electronic, EPR, magnetic and mass spectral studies of mono and homo-binuclear Co(II) and Cu(II) complexes with a novel macrocyclic ligand. Spectrochimica Acta Part A **62**, 1102–1106 (2005)

24. Rosokha, S.V., Lampeka, Y.D., Matoshtan, I.M.: Synthesis and properties of a new series of bis(macrocyclic) dicopper(II,II), dinickel(II,II) and dinickel(III,III) complexes based on the 14-membered pentaaza unit. J. Chem. Soc., Dalton Trans. 631–636 (1993)

25. Nakamoto, K.: Infrared Spectra of Inorganic and Coordination Compounds. Wiley Interscience, New York (1970)

26. Lever, A.B.P.: Inorganic Electronic Spectroscopy. Elsevier, Amsterdam (1984)

27. Cotton, F.A.: Wilkinson, Advanced Inorganic Chemistry, 5th edn. Wiley, New York (1988)

28. Varkey, S.P., Ratnasamy, C., Ratnasamy, P.: Zeolite-encapsulated manganese(III)salen complexes. J. Mol. Catal. A: Chem. **135**, 295–306 (1998)