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

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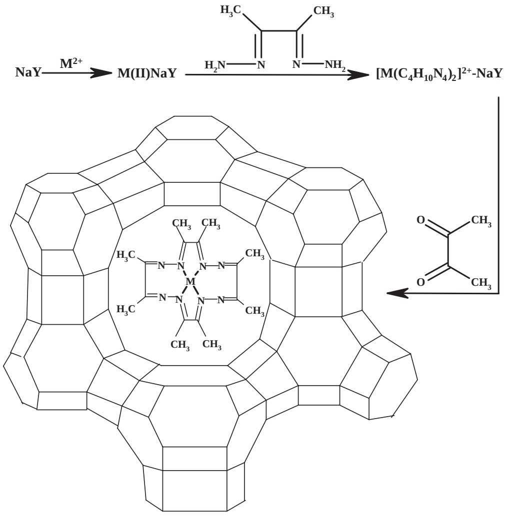
Nanodimensional pores of zeolite-Y (host) encapsulated Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) complexes of unsaturated 16-membered octaaza–macrocycle (guest), 3,4,7,8,11,12,15,16-octamethyl-1,2,5,6,9,10,13,14-octaaza[16]annulene "Me_8-[16]aneN_8", were synthesized and characterized.

One of the most attractive properties of zeolites is their well organized nanopores and nanochannels which serve readily as supporting hosts for various molecules. Encapsulation of catalytically active transition-metal complexes inside the nanopores of zeolites, "ship-in-a-bottle," has been believed to be one of the most promising strategies in the development of viable industrial catalysts.[1]

In previous paper, we reported a series of complexes with polyaza macrocyclic ligands, by the template condensation of diamine, formaldehyde, and amine in the presence of metal salt.[2] In this paper, I have reported the synthesis and characterization of metal(II) complexes of unsaturated 16-membered octaaza "Me_8[16]aneN_8" macrocycle ligands "3,4,7,8,11,12,15,16-octamethyl-1,2,5,6,9,10,13,14-octaaza[16]annulene, [M(Me_8-[16]aneN_8)]$(ClO_4)_2$ (M = Mn(II), Co(II), Ni(II), Cu(II), and Zn(II)),[9] encapsulated within the nanocavities of Y-zeolite by the template reactions of butane-2,3-dione dihydrazone with biacetyl, $[M(Me_8[16]aneN_8)]^{2+}$–NaY, shown in Scheme 1.[7,10] Instrumental details for neat and encapsulated complexes are the same as described earlier.[3]

The results of chemical analyses of the samples are given in Table 1. 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 formulae of metal-exchanged zeolites showed a metal dispersion of around 11 moles per unit cell (MnNaY, $Na_{33.2}Mn_{11.3}[(AlO_2)_{56}(SiO_2)_{136}]\cdot nH_2O$; CoNaY, $Na_{34}Co_{11}[(AlO_2)_{56}(SiO_2)_{136}]\cdot nH_2O$; NiNaY, $Na_{33.8}Ni_{11.1}[(AlO_2)_{56}(SiO_2)_{136}]\cdot nH_2O$; CuNaY, $Na_{34.4}Cu_{10.8}[(AlO_2)_{56}(SiO_2)_{136}]\cdot nH_2O$; ZnNaY, $Na_{33}Zn_{11.4}[(AlO_2)_{56}(SiO_2)_{136}]\cdot nH_2O$). The analytical data of each complex indicated M:C:H molar ratios almost close to calculated for the mononuclear structure. The Si and Al contents in metal-exchanged zeolites and the zeolite complexes were almost the same as parent zeolite. This indicate little changes in the zeolite framework due to the absence of dealumination in metal ion exchange. The X-ray diffraction patterns of zeolite-containing Me_8[16]aneN_8 complexes were similar to metal-exchanged zeolites and the parent NaY zeolite. The zeolite crystallinity was retained on encapsulating Me_8[16]aneN_8 complexes. The SEM photographs of the samples taken before Soxhlet extraction, showed the deposition of complexes on the external surface. However, the absence of extraneous materials in the SEM photographs of finished products indicated the complete removal of surface complexes, which could be accomplished by extended extraction procedure.



M = Mn(II), Co(II), Ni(II), Cu(II), Zn(II)

Scheme 1.

Surface area and pore volume values estimated by the low-temperature nitrogen adsorption at relative pressures (P/P_0) in the range 0.05–0.9 are given in Table 1. There was a drastic reduction of surface area and pore volume of zeolites on encapsulating the metal complexes. Since the zeolite framework structure is not affected by encapsulation as shown by the XRD patterns, the reduction of surface area and pore volume provides direct evidence for the presence of complexes in the cavities.[4]

The infrared spectra of the complexes, "[Ni(Me_8[16]aneN_8)]$(ClO_4)_2$" were all very similar to each other and support the ligand structure proposed in Scheme 1. The IR bands of zeolite-encapsulated transition metal complexes occurred at the frequencies shifted within $\approx$5–10 cm^{-1} in comparison with free complex; furthermore, some changes in band intensities were observed in the region of the C=N stretching vibration.

Comparing the magnetic measurement obtained at room temperature and electronic spectra (Table 1) of metal complexes with square-planer M(II) Schiff-base tetraaza–macrocycle complexes indicated that the octaaza–ligands of this study do not differ significantly from the tetraaza–ligands with respect to the ligand field strength.[5] Bands due to zeolite encapsulated metal(II) complex appeared at 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.

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Table 1. Chemical composition, magnetic and conductance data, UV–vis and DRS absorption, surface area, pore volume, and IR stretching frequencies of neat and zeolite-encapsulated[a]

Sample	C%	H%	N%	M%	C/N	Si%	Al%	Na%	Si/Al	$\nu_{C=N}$[e] KBr /cm^{-1}	d↔d/ cm^{-1}	μ_B	Λ_M[b] /S^{-1}cm^{-2} mol	Surface area[c] /m^2 g^{-1}	Pore volume[d] /mL g^{-1}
NaY	—	—	—	—	—	21.76	8.60	7.50	2.53	—	—	—	—	545	0.31
MnNaY	—	—	—	2.58	—	22.08	8.73	3.34	2.53	—	—	—	—	535	0.30
[Mn(Me$_4$[16]aneN$_8$)](ClO$_4$)$_2$	33.00	4.15	19.24	9.43	1.72	—	—	—	—	1613	23,350[b]	1.78	265	—	—
	(32.76)	(4.01)	(19.35)	(9.28)	(1.69)										
[Mn(Me$_4$[16]aneN$_8$)]$^{2+}$–NaY	2.63	1.52	1.72	2.26	1.53	21.78	8.61	5.39	2.53	1607	23,640	—	—	398	0.24
CoNaY	—	—	—	3.71	—	21.53	8.53	3.36	2.53	—	—	—	—	532	0.30
[Co(Me$_4$[16]aneN$_8$)](ClO$_4$)$_2$	32.77	4.13	19.11	10.05	1.71	—	—	—	—	1614	22,670[b]	1.75	247	—	—
	(32.50)	(3.96)	(19.30)	(9.86)	(1.68)										
[Co(Me$_4$[16]aneN$_8$)]$^{2+}$–NaY	2.61	1.51	1.67	2.34	1.56	21.24	8.40	5.38	2.53	1609	22,930	—	—	396	0.24
NiNaY	—	—	—	3.72	—	21.79	8.62	3.28	2.53	—	—	—	—	528	0.31
[Ni(Me$_4$[16]aneN$_8$)](ClO$_4$)$_2$	32.79	4.13	19.12	10.01	1.71	—	—	—	—	1617	23,190[b]	−0.04	253	—	—
	(32.51)	(3.97)	(19.28)	(9.83)	(1.69)										
[Ni(Me$_4$[16]aneN$_8$)]$^{2+}$–NaY	2.53	1.48	1.61	2.31	1.57	19.80	7.83	5.34	2.53	1610	23,460	—	—	397	0.24
CuNaY	—	—	—	3.86	—	21.48	8.49	3.28	2.53	—	—	—	—	532	0.30
[Cu(Me$_4$[16]aneN$_8$)](ClO$_4$)$_2$	32.52	4.09	18.96	10.75	1.72	—	—	—	—	1620	16,420[b]	1.77	249	—	
	(32.29)	(3.83)	(19.15)	(10.51)	(1.69)										
[Cu(Me$_4$[16]aneN$_8$)]$^{2+}$–NaY	2.50	1.43	1.67	2.81	1.50	21.07	8.33	5.33	2.53	1610	16,650	—	—	397	0.24
ZnNaY	—	—	—	3.96	—	22.30	8.83	3.32	2.53	—	—	—	—	534	0.31
[Zn(Me$_4$[16]aneN$_8$)](ClO$_4$)$_2$	32.42	4.08	18.90	11.03	1.72	—	—	—	—	1615	—	—	—	—	—
	(32.21)	(3.80)	(19.11)	(10.89)	(1.69)										
[Zn(Me$_4$[16]aneN$_8$)]$^{2+}$–NaY	2.42	1.39	1.59	2.84	1.52	21.93	8.67	5.34	2.53	1611	—	—	—	404	0.25

[a]Estimated values are given in parentheses. [b]In nitromethane solutions at at 25 °C unless otherwise specified. [c]Surface area is the "monolayer equivalent area" calculated as explained in the Ref. 8. [d]Calculated by the *t*-method. [e]Vibrational stretching of coordinated C=N.

In summary, the results show that new square-planer octaaza "[M(Me$_8$[16]aneN$_8$)]$^{2+}$" can be encapsulated in the nanodimensional pores of zeolite by template condensation between pre-entrapped [M(C$_4$H$_{10}$N$_4$)$_2$]$^{2+}$ complexes with biacetyl.

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9 Typical procedure for [M(Me$_8$[16]aneN$_8$)](ClO$_4$)$_2$ (M = Mn(II), Co(II), Ni(II), Cu(II), and Zn(II)) complexes; to a stirred methanol solution (500 mL) of metal(II) percholorate (42.07 mmol) were slowly added 9.61 g of butane-2,3-dione dihydrazone (the Schiff-base was prepared by the method of Bush and Bailar,[6] and biacetyl (7.25 g, 84.20 mmol). The mixture was heated at reflux for 24 h. The solution was cooled to room temperature and filtered to remove metal hydroxide. The filtrate was kept in the refrigerator until solid formed. The solid were filtered, washed with diethyl ether, and air-dried. The products were crystallized from hot water.

10 For preparation of [M(Me$_8$[16]aneN$_8$)]$^{2+}$–NaY; to a stirred methanol solution of M(II)NaY[7] (4 g) was added 0.45 g of butane-2,3-dione dihydrazone suspended in 100 mL of methanol and then refluxed for 8 h. The solid consisting of [M(C$_4$H$_{10}$N$_4$)$_2$]$^{2+}$ denoted as [M(C$_4$H$_{10}$N$_4$)$_2$]$^{2+}$–NaY was collected by filtration, washed with ethanol and then dried at 80 °C under vacuum for 14 h. To a stirred methanol suspension (100 mL) of [M(C$_4$H$_{10}$N$_4$)$_2$]$^{2+}$–NaY (2 g) were slowly added biacetyl (0.5 mL). The mixture was heated at reflux for 24 h. The solution was filtered and the resulting zeolites, were Soxhlet extracted with *N*,*N*′-dimethylformamide (for 4 h) and then with ethanol (for 3 h) to remove excess unreacted products from by-product and any metal complexes adsorbed onto the external surface of the zeolite crystallites. The resulting solids were dried at 90 °C under vacuum for 12 h. The remaining bis-(butane-2,3-dione dihydrazone)metal(II) ions in zeolite were removed by exchanging with aqueous 0.1 M NaNO$_3$ solutions.

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