Nanodimensional Microreactor-encapsulation of 18-Membered Decaaza Macrocycle Copper(II) Complexes

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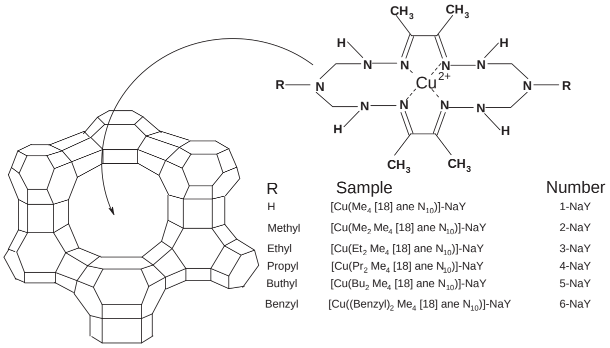
Copper(II) complexes of 18-membered decaaza macrocyclic ligands “1,10-dialkyl-5,6,14,15-tetramethyl-1,3,4,7,8,10,12,13,16,17-decaazacyclooctadecane” [Cu(R_2 Me_4 [18] ane N_{10})](ClO_4)$_2$ (R = H, Me, Et, Pr, Bu, Benzyl), have been prepared from the one-pot template condensation reaction of formaldehyde, 2,3-butanedihydrazone with alkyl and benzyl amine in the presence of copper(II) ion within the nanodimensional pores of zeolite Y.

Coordination geometry and properties of most transition metal complexes of 14-membered polyaza macrocyclic ligands containing primary amine have been studied.[2–6] However, most of them were tetraaza macrocyclic ligands, and 18-membered macrocyclic ligands containing ten nitrogen atoms in the nanodimensional pores of zeolite Y have not been reported to date. I have been interested in the synthesis of various types of polyaza macrocyclic complexes containing primary amino alkyl groups from “one-pot template” condensation reactions in supercage of zeolite. 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 nanodimensional pores 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 of alkenes, alkanes, and alcohol.[7–10] In the appropriate molecular sieve host, the metal complex should be free to move about within the confines of the cavities but prevented from leading by restrictive pore openings. Hence the term zeolite “ship-in-a-bottle” complex may be applied.

In previous paper, I reported a series of complexes with polyaza macrocyclic ligands, by the template condensation of diamine, formaldehyde, and amine in the presence of metal salt.[11] In this paper, I report the synthesis and characterization of copper(II) complexes of 18-membered decaaza macrocyclic ligands encapsulated within the cavities of Y-zeolite by the one-pot template reactions.[1]

The “Flexible Ligand Synthesis” (FLS) lead to the encapsulation of Cu(II) complexes of decaaza ligand inside the zeolite pore. 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 formula of metal-exchanged zeolites show a copper dispersion of 10.81 moles per unit cell ($Na_{34.4}Cu_{10.81}[(AlO_2)_{56}(SiO_2)_{136}]\cdot nH_2O$). The analytical data of each complex indicate Cu:C:N molar ratios almost close to those calculated for the mononuclear structure.

The chemical compositions (Table 1) confirmed the purity and stoichiometry of the neat and zeolite-encapsulated complexes. The chemical analyses of the samples reveal the presence of organic matter with an C/N ratio roughly similar to that for neat complexes. In Table 1 the mol ratios Si/Al obtained by chemical analysis for zeolite are presented. The Si and Al contents in Cu(II)–NaY 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 de-alumination in metal ion exchange. The X-ray diffraction patterns of zeolite contained decaaza complexes are similar to those of Cu(II)–NaY and the parent NaY zeolite.



R	Sample	Number
H	[Cu(Me_4 [18] ane N_{10})]-NaY	1-NaY
Methyl	[Cu(Me_2 Me_4 [18] ane N_{10})]-NaY	2-NaY
Ethyl	[Cu(Et_2 Me_4 [18] ane N_{10})]-NaY	3-NaY
Propyl	[Cu(Pr_2 Me_4 [18] ane N_{10})]-NaY	4-NaY
Buthyl	[Cu(Bu_2 Me_4 [18] ane N_{10})]-NaY	5-NaY
Benzyl	[Cu((Benzyl)$_2$ Me_4 [18] ane N_{10})]-NaY	6-NaY

Scheme 1.

The IR bands of zeolite-encapsulated copper(II) complexes occur at frequencies shifted within $\approx 4\,cm^{-1}$ from those of the free complex; furthermore, some changes in band intensities can be observed in the region of the N–H stretching vibration. These observation not only confirm the presence of copper(II) complex of 18-membered decaaza macrocycle in the zeolite, but also suggest that its structure is not identical to that of the neat complex, thus, stereochemically induced distortion of the complex, chemical ligation of the zeolite framework (NaY can act as a strong ligand), or some host–guest interactions (electrostatic) with the zeolite, can not be ruled out.[13] The five entrapped complexes exhibit very similar IR spectra with bands at all regions that are shifted $\approx 4\,cm^{-1}$ relative to those of the corresponding free complexes.[11] These vibrations in band frequency can also be attributed to (i) distortions of the complexes, or to (ii) interactions with the zeolite matrix (by electrostatic effects or coordination—the higher negative charge of the zeolite host makes it a strong ligand; Table 1).

Electronic data for neat and encapsulated copper(II) complexes within the nanodimensional pores of zeolite Y are summarized in Table 1. Bands due to zeolite encapsulated copper(II) complex appear at $16654\,cm^{-1}$, and charge transfer bands appear in the near-UV region; these values are very similar to those obtained for the discrete complex in Nujol and as a single crystal.[14] Surface area and pore volume values estimated by the low-

Table 1. Chemical composition, DRS absorption surface area and pore volume data and IR stretching frequencies of neat and zeolite-encapsulated copper(II) complexes[a]

Sample	C%	H%	N%	C/N	Si%	Al%	Na%	Cu%	Si/Al	$\nu_{N\text{–}H}$ /cm^{-1}	d↔d /cm^{-1}	$\nu_{C=N}$ /cm^{-1}	Surface area /m^2/g	Pore volume /mL/g
NaY					21.76	8.60	7.50	—	2.53				545	0.31
CuNaY					21.45	8.48	4.47	3.86	2.53				532	0.30
[Cu($C_4H_{10}N_4$)$_2$] (ClO_4)	19.58	4.11	22.82	0.86				12.95			16340[b]	1617		
[Cu($C_4H_{10}N_4$)$_2$] NaY	3.08	1.13	3.38	0.91	21.34	8.44	5.45	2.85	2.53		16380	1614	415	0.25
1	25.17 (24.31)	4.54 (4.49)	24.46 (24.51)	1.03 (0.99)				11.10 (10.97)		3285	16393[b]	1616		
1-NaY	3.95	1.15	4.30	0.92	21.35	8.44	5.46	2.84	2.53	3283	16654	1615	393	0.23
2	28.01 (27.81)	5.02 (4.90)	23.31 (24.06)	1.02 (1.16)				10.58 (10.46)		3280	16339[b]	1615		
2-NaY	5.64	1.64	5.08	1.11	21.33	8.43	5.44	2.83	2.53	3280	16584	1614	310	0.22
3	30.57 (30.41)	5.41 (5.29)	22.27 (22.36)	1.37 (1.36)				10.11 (10.01)		3280	16380[b]	1612		
3-NaY	7.29	2.12	5.88	1.24	21.35	8.44	5.46	2.84	2.53	3283	16670	1615	297	0.22
4	39.93 (39.72)	5.79 (5.67)	21.32 (21.43)	1.87 (1.53)				9.67 (9.56)		3275	16420[b]	1610		
4-NaY	8.97	2.61	6.32	1.42	21.38	8.45	5.43	2.83	2.53	3272	16720	1610	284	0.21
5	35.09 (34.60)	6.17 (6.03)	20.45 (20.73)	1.72 (1.67)				9.34 (9.27)		3270	16367[b]	1610		
5-NaY	9.76	2.85	6.38	1.53	21.43	8.47	5.42	2.82	2.53	3271	16616	1611	272	0.20
6	41.47 (41.37)	5.09 (4.78)	18.60 (18.88)	2.23 (2.19)				8.22 (8.14)		3290	16447[b]	1620		
6-NaY	6.48	1.88	3.12	2.08	21.40	8.46	5.45	2.84	2.53	3295	16707	1623	254	0.17

[a]Estimated values are given in parentheses. [b]In aqueous solutions at 25 °C unless otherwise specified.

temperature nitrogen adsorption at relative pressures (P/P_0) in the range 0.05–0.90 are given in Table 1. There is a drastic reduction of surface area and pore volume of zeolites on encapsulation of the copper(II) complexes. Since the zeolite framework structure is not affected by encapsulation as shown by the XRD pattern, the reduction of surface area and pore volume provides direct evidence for the presence of complexes in the cavities.[15]

In summary, the results show that [Cu(R$_2$ Me$_4$ [18] ane N$_{10}$)]$^{2+}$ can be encapsulated in the nanodimensional pores of zeolite by in situ template condensation between pre-entrapped [Cu($C_4H_{10}N_4$)$_2$]$^{2+}$ complexes, formaldehyde and the corresponding amine.

References and Notes

1 The neat complexes were prepared according to the procedure described previously.[11b] For preparation of [Cu($C_4H_{10}N_4$)$_2$]$^{2+}$–NaY; to a stirred methanol solution of Cu–NaY (4 g) was added 0.37 g of 2,3-butanedihydrazone (the Schiff-base was prepared by the method of Bush and Bailar.[12]) suspended in 100 mL of methanol and then refluxed for 8 h. The light blue solid consisting of [Cu($C_4H_{10}N_4$)$_2$]$^{2+}$ denoted as [Cu($C_4H_{10}N_4$)$_2$]$^{2+}$–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 [Cu($C_4H_{10}N_4$)$_2$]$^{2+}$–NaY (2 g) were slowly added 36% formaldehyde (9 mL) and amine (ammonia, methylamine, ethylamine, propylamine, isobutylamine, benzylamine) (3.75 mmol). The mixture was heated at reflux for 24 h until a pale blue suspension resulted. 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 amine–aldehyde condensation and any Cu(II) complexes adsorbed onto the external surface of the zeolite crystallites. The resulting pale-blue solids were dried at 90 °C under vacuum for 12 h. The remaining bis(2,3-butanedihydrazone) copper(II) ions in zeolite were removed by exchanging with aqueous 0.1 M $NaNO_3$ solutions.

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