

Zeolite-encapsulation copper(II) complexes with 14-membered hexaaza macrocycles: synthesis, characterization and catalytic activity

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Abstract

Copper(II) complexes with 14-membered hexaaza macrocyclic ligand “1,3,6,8,10,13-hexaaza cyclotetradecane, 1,8-dimethyl-“[Cu((Me)₂[14]aneN₆)](ClO₄)₂” **2**; 1,8-diethyl-“[Cu((Et)₂[14]aneN₆)](ClO₄)₂” **3**; 1,8-dibutyl-“[Cu((Bu)₂[14]aneN₆)](ClO₄)₂” **4**; and 1,8-dibenzyl-1,3,6,8,10,13-hexaazacyclotetradecane-“[Cu((benzyl)₂[14]aneN₆)](ClO₄)₂” **5**”, have been prepared by the one-pot template reactions of formaldehyde and ethylenediamine with alkyl and benzyl amine within the cavities of zeolite Y. These complexes were entrapped in the supercage of zeolite Y by a two-step process in the liquid phase: (i) inclusion of a Cu(II) precursor complex, [Cu(en)₂]²⁺-NaY **8**, and (ii) in situ one-pot template reaction of the copper(II) precursor complex with the formaldehyde and amine. The new materials “[Cu((Me)₂[14]aneN₆)]-NaY **9**, [Cu((Et)₂[14]aneN₆)]-NaY **10**, [Cu((Bu)₂[14]aneN₆)]-NaY **11**, [Cu((Benzyl)₂[14]aneN₆)]-NaY **12**” were characterized by several techniques: chemical analysis and spectroscopic methods (FT-IR, UV-Vis, XRD, BET, DRS). Analysis of the data indicates that the Cu(II) complexes are encapsulated in the NaY zeolite supercages and exhibit different from those of the free complexes, which can arise from distortions caused by steric effects due to the presence of sodium cations, or from interactions with the zeolite matrix. By comparing the performance of the heterogeneous system with the neat complex in the oxidation of tetrahydrofuran (THF) using hydrogen peroxide as oxygen donor, a protection effect of the matrix over the active center was evidenced by a higher conversion and product selectivity. Encaged complexes yield mainly tetrahydrofuran-2-ol (THF-2-ol) and insignificant amount of tetrahydrofuran-2-one (THF-2-one), while with their homogeneous counterparts, selectivity's to THF-2-one are higher.

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1. Introduction

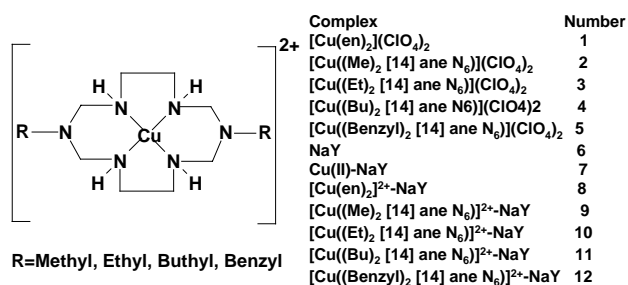
Transition metal ions exchanged with zeolites have been used frequently in catalytic oxidative functionalization of C–H bands either α to a double bond (allylic position) or of a saturated hydrocarbon [1–6]. The key point in designing of such catalysis systems are based on the remarkable ability of Cytochrome P-450 to active dioxygen with resultant oxygen transfer to unreactive C–H bonds of organic substrates [7]. In recent years, oxidation of ethers catalytically and photochemically with the formation of corresponding esters or acids have been reported [8–10]. We envisaged that similar oxidation with H₂O₂ and TBHP in the presence of

our recent reported zeolite catalysis system can be efficiently carried out under mild conditions [11,12].

In this paper, we report the synthesis and characterization of copper(II) complexes of 14-membered hexaaza macrocyclic ligand “1,3,6,8,10,13-hexaazacyclotetradecane, 1,8-dimethyl-“[Cu((Me)₂[14]aneN₆)](ClO₄)₂” **2**; 1,8-diethyl-“[Cu((Et)₂[14]aneN₆)](ClO₄)₂” **3**; 1,8-dibutyl-“[Cu((Bu)₂[14]aneN₆)](ClO₄)₂” **4**; and 1,8-dibenzyl-1,3,6,8,10,13-hexaazacyclotetradecane-“[Cu((benzyl)₂[14]aneN₆)](ClO₄)₂” **5**”, encapsulated within the cavities of zeolite Y by the one-pot template reactions of formaldehyde and ethylenediamine with alkyl and benzyl amine “[Cu((Me)₂[14]aneN₆)]-NaY **9**, [Cu((Et)₂[14]aneN₆)]-NaY **10**, [Cu((Bu)₂[14]aneN₆)]-NaY **11**, [Cu((benzyl)₂[14]aneN₆)]-NaY **12**”, shown in Scheme 1, and used in the oxidation of tetrahydrofuran (THF) with hydrogen peroxide as oxygen donor.

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Scheme 1.

2. Experimental

2.1. Materials

All the solvent was purchased from Merck (pro-analysis) and was dried using molecular sieves (Linda 4 Å), methylamine, ethylamine, *iso*-butylamine, benzylamine, formaldehyde, ethylenediamine, hydrogen peroxide were obtained from Merck. Tetrahydrofurane were purified by standard procedure [13]. NaY (with a Si:Al ratio of 2.53) was purchased from Aldrich (lot No. 67812). The complex [Cu(en)₂](ClO₄)₂ was prepared according to the published procedures [14].

2.2. Physical measurements

After completely destroying the zeolitic framework with hot and concentrated HCl, sodium, aluminum and copper were analyzed by atomic absorption spectrophotometer (AAS, Perkin-Elmer 4100-1319) and SiO₂ was determined by gravimetric analysis. FT-IR spectra were recorded on Shimadzu Varian 4300 spectrophotometer in KBr pellets. The electronic spectra of the neat complexes 1–5 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 the range 1500–200 nm, using MgO as reference. The elemental analysis (carbon, hydrogen and nitrogen) 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. BET surface area and total pore volume were measured by nitrogen adsorption at liquid nitrogen temperature using a Micromeritics Gemini 2360 analyzer.

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 catalyst. The products were analyzed by GC-MS, using a Philips Pu 4400 Chromatograph (1.5 m, 3% OV-17 Column), Varian 3400 Chromatograph (25 m, DB-5 Column) coupled with a QP Finnegan MAT INCOF 50, 70 eV.

2.3. Sample preparation

2.3.1. Preparation of neat complexes (2–5)

The neat complexes as catalysts were prepared according to the procedure described previously [15,16].

2.3.2. Preparation of Cu(II)-NaY (7)

A 2 g NaY zeolite was suspended in 100 ml distilled water, which contained copper(II) nitrate (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 content and dried for 10 h at 80 °C under vacuum.

2.3.3. Preparation of [Cu(en)₂]²⁺-NaY (8)

Typically a 4 g sample of NaY zeolite was mixed with 0.37 g of bis(ethylenediamine)copper(II)perchlorate (1), suspended in 100 ml of methanol and then refluxed for 8 h. The pale blue solid consisting of [Cu(en)₂]²⁺ exchanged with Na⁺ in NaY and denoted as [Cu(en)₂]²⁺-NaY was collected by filtration, washed with ethanol and then dried at 80 °C under vacuum for 14 h.

2.3.4. Preparation of [Cu(R₂[14]aneN₆)]²⁺-NaY (R = H, Me, Et, butyl, benzyl) (9–12)

To a stirred methanol suspension (100 ml) of 8 (2 g) were slowly added 36% formaldehyde (9 ml) and amine (methylamine, ethylamine, *iso*-butylamine, benzyl amine) (3.75 mmol). The mixture was heated at reflux for 24 h until a pale orange 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-orange solids were dried at 90 °C under vacuum for 12 h.

2.4. Oxidation of tetrahydrofurane; general procedure [17]

In a typical procedure, a mixture of catalyst (0.5 g) and tetrahydrofurane (0.05 mol) was stirred in a 50 ml round bottom two-necked flask equipped with a condenser and dropping funnel for 30 min, under nitrogen atmosphere. Then 0.05 mol of the oxidant (H₂O₂, 30% in H₂O) was added through the dropping funnel. The mixture was then refluxed for 8 h. After filtration and washing with solvent, the filtrate was subjected to GC and GC-MS.

3. Results and discussion

3.1. Synthesis and characterization

Coordination geometry and properties of most transition metal complexes with 14-membered hexaaza macrocyclic

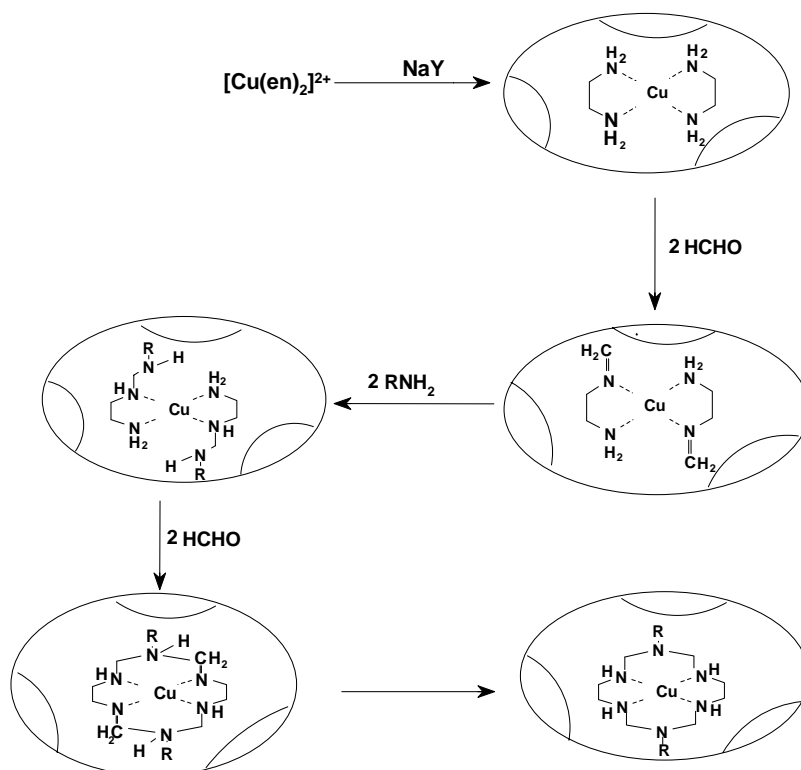
ligands containing primary amine have been studied [18–21]. However, most of them were tetraaza macrocyclic ligands, and 14-membered macrocyclic ligands containing six nitrogen atoms in the fully saturated macrocyclic framework within the cavities of zeolite have been to some extent reported to date. We 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.

Synthesis of 14-membered hexaaza macrocycle copper(II) encapsulated complexes in zeolite (9–12) was carried out by a stepwise method. Ratnamy and co-workers described this process as “flexible ligand method” [22]. The bis(ethylenediamine)copper(II) exchanged NaY zeolite (8) was prepared by exchanging Na^+ of NaY with 0.01 M solutions of **1** in methanol solution. Refluxing of the **8** with formaldehyde and R-NH₂ for about 24 h effected template formation of the 14-membered hexaaza macrocyclic in the cavity followed by complex formation with metal ion (Scheme 2). The crude mass was finally purified by Soxhlet extraction method. The remaining bis(ethylenediamine)copper(II) ions in zeolite were removed by exchanging with aqueous 0.1 M NaCl solution.

The flexible ligand synthesis (Scheme 2) lead to the encapsulation of Cu(II) complexes of hexaaza 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 $\text{Na}_{56}[(\text{AlO}_2)_{56}(\text{SiO}_2)_{136}]$. Metal ion exchange at 39% in zeolite. The unit cell formula of metal-exchanged zeolites show a copper dispersion of 10.8 moles per unit cell ($\text{Na}_{34.4}\text{Cu}_{10.8}[(\text{AlO}_2)_{56}(\text{SiO}_2)_{136}] \cdot n\text{H}_2\text{O}$). The analytical data of each complex indicate Cu:C:N molar ratios almost close to those calculated for the mononuclear structure. However, the presence of minute traces of free $[\text{Cu}(\text{en})_2]^{2+}$ in the lattice could be assumed as the $[\text{Cu}(\text{en})_2]^{2+}$ content is slightly higher than the stoichiometric requirement only a portion of $[\text{Cu}(\text{en})_2]^{2+}$ in exchanged zeolite has undergone complexation and the rest is expected to be removed on re-exchange with sodium nitrate solution.

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 N/C 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 CuNaY and the zeolite complexes are almost in 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 hexaaza complexes are similar to those of CuNaY and the parent NaY zeolite. The zeolite crystallinity is retained on encapsulating complexes. Crystalline phase of free metal ions or encapsulation ligand complexes were not detected in any of the patterns



Scheme 2.

Table 1

Chemical composition, DRS absorption and IR stretching frequencies of neat and zeolite-encapsulated copper(II) complexes

Sample	C (%)	H (%)	N (%)	C/N	Si (%)	Al (%)	Na (%)	Cu (%)	Si/Al	$\nu_{\text{N-H}}$ (cm^{-1})	$d \leftrightarrow d$ (cm^{-1})
6	–	–	–	–	21.76	8.60	7.50	–	2.53	–	–
7	–	–	–	–	21.48	8.48	4.454	3.86	2.53	–	–
1	12.55 (12.47)	4.21 (4.13)	14.64 (14.71)	0.86 (0.85)	–	–	–	–	–	–	–
8	0.27	3.11	0.31	0.87 (0.89)	21.32	8.43	5.44	2.87	2.53	–	17600
2	24.37 (24.22)	5.32 (5.30)	17.05 (16.96)	1.43 (1.43)	–	–	–	–	–	3212	20576
9	0.67	3.15	0.47	1.42 (1.45)	21.19	8.38	5.41	2.86	2.53	3209	19455
3	27.57 (27.32)	5.81 (5.86)	16.13 (15.65)	1.72 (1.75)	–	–	–	–	–	3232	20618
10	0.66	3.18	0.46	1.43 (1.44)	21.15	8.36	5.39	2.85	2.53	3228	19379
4	33.31 (32.21)	6.64 (6.53)	14.57 (14.63)	2.29 (2.27)	–	–	–	–	–	–	–
11	1.06	3.09	0.46	2.30 (2.32)	21.09	8.34	5.38	2.84	2.53	3214	19268
5	40.97 (40.86)	5.31 (5.27)	3.14 (3.10)	–	–	–	–	–	–	–	–
12	1.45	3.19	0.46	3.15 (3.16)	21.01	8.31	5.36	2.83	2.53	3217	19841

Estimated values are given in parentheses. In nitromethane solutions at 25 °C.

as their fine dispersion in zeolite might have rendered them non-detectable by XRD.

IR spectroscopy can provide information on the encapsulated metal complexes and on the crystallinity of the host zeolite. The spectra of all samples are dominated by bands due to the zeolite [23], (surface hydroxyl groups, ν_{OH} , in the range 3700–3300 cm^{-1} ; lattice vibrations in the range 1300–450 cm^{-1}), even though the presence of copper(II) complexes can be detected (Table 1). No significant dealumination or expansion of the cavities took place, as the zeolite structure-sensitive vibrations (e.g. the asymmetric stretch at 1130 cm^{-1} and the symmetric stretch at 810 cm^{-1}) did not shift or broaden significantly upon inclusion of the complexes. This result supports the observation that the encapsulation process does not modify the zeolite framework.

The bands due to the complexes are weaker (due to a low concentration of the complexes) and thus can only be observed in the regions where the zeolite matrix does not absorb, i.e. from 1200 to 1620 cm^{-1} . The IR bands of 9–12 occur at frequencies shifted within 5–8 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 observations not only confirm the presence of copper(II) complex of 14-membered hexaaza 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 [24,25]. The five entrapped complexes exhibit very similar IR spectra with bands at all regions that are shifted 5–8 cm^{-1} relative to those of the corresponding free complexes [15,16]. 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 cavity of zeolite Y are summarized in

Table 1. Bands due to **8** appear at 17,600 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 [26]. Electronic spectra of the five encapsulated 14-membered hexaaza macrocycle complexes are very similar and show $d \leftrightarrow d$ bands in the visible region: again, they are also similar to those obtained for the corresponding discrete complexes and to those of other N_6 macrocycle copper(II) complexes [27–29].

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 2. There is a drastic reduction of surface area and pore volume of zeolites on encapsulating 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 [30].

3.2. Catalytic activity

One of the major drawbacks of homogeneous metal complexes as catalysts is their irreversible deactivation due to formation of μ -oxo and μ -peroxo dimeric and other polymeric species especially when using oxidant. Since the formation of these bulky dimeric/polymeric species is sterically impossible when the monomeric complex is encapsulated

Table 2
Surface area and pore volume data

Sample	Surface area (m^2/g)	Pore volume (ml/g)
6	453	0.31
7	532	0.30
8	490	0.30
9	412	0.25
10	395	0.24
11	362	0.22
12	339	0.21

Table 3

Substrate conversions and product selectivities in the oxidation of tetrahydrofuran with H₂O₂ in the presence of 14-membered hexaaza macrocyclic copper(II) complexes

Catalyst	Conversion (%)	Yield (%)		
		THF-2-one	THF-2-ol	4-Hydroxy butyraldehyde
1	38.6	47.1	29.7	23.2
2	58.6	76.5	16.7	6.8
3	61.4	81.6	13.6	4.8
4	71.5	84.3	10.5	5.2
5	98.6	100	–	–

and physical confined within the supercages of zeolite Y, it was anticipated that encapsulated catalysts would be more rugged and can be recycled for use. The data in Tables 3 and 4 support the above hypothesis. As mentioned earlier, the neat complexes could not be recycled even once as they lost their catalytic activity after use. By contrast, the encapsulated, solid catalysts could be filtered, washed with a solvent and reused without major loss in activity.

In our recent publications, we reported the role of some transition metals and their complexes included within zeolite Y and supported on alumina as catalysts in the activation of C–H bond [11,12,16,17]. In both cases, it was observed that these catalysts were able to transfer oxygen from TBHP to substrate and hydroxylate the hydrocarbons. Since the oxidation of tetrahydrofuran in the presence of titanium silicate and H₂O₂ [8] or photochemically with benzil and dioxygen [10] was shown to lead almost to the corresponding lactones, we decided to investigate these oxidation reactions systems.

Tables 3 and 4 shows the substrate conversion and product percentages of oxidation of tetrahydrofuran with H₂O₂ in the presence of 1–12. These values are similar or slightly higher than those obtained with CrO₃, Pb(CH₃COO)₄ [31], RuO₄ in the presence of OCl[–] or IO₄[–] [32], titanium silicates (TS-1, TS-2) [33], Co(II) porphyrin [34] and iron(III) and manganese(II) bipyridine complexes included in zeolite Y and bentonite [17].

Results of Table 3 show the catalytic activity of homogeneous catalysts 1–5. Comparing between neat 1–5 and

zeolite encapsulated complexes 8–12 as catalyst evidence that zeolite-encapsulated catalysts gave higher conversion of THF than their corresponding neat complexes. The higher activity of encapsulated complexes is because of site isolation of the complexes.

The selectivity and activity of these zeolite-encapsulated catalysts on the oxidation of tetrahydrofuran with H₂O₂ are given in Table 3. At the end of reaction, the catalyst was separated by filtrations, thoroughly washed with solvent and reused under similar conditions by atomic absorption spectroscopy showed no reduction in the amount of copper; they exhibited a slightly lower catalytic activities (0.20%).

Decrease of the conversion in both systems (homogeneous and heterogeneous catalysts) after 8 h of reaction is noticeable. Deactivation of the homogeneous catalyst is due to structural damage as evidenced by UV-Vis spectra; in the heterogeneous catalyst the apparent deactivation is not caused by destruction of the active center but by the trapping of substrate and products of reaction within the zeolite, as also found by Herron [35]. These compounds were released, identified, quantified and added to the products previously found in the heterogeneous reaction solution at 24 h. Tables 2 and 3 show the yields obtained with each catalytic system for the different products. As for product distribution, the reaction solutions of neat complex gave THF-2-one > THF-2-ol > 4-hydroxybutyraldehyde while product distribution for encapsulated complex gave THF-2-ol > THF-2-one > 2,3-dihydroxytetrahydrofuran.

4. Conclusions

The results show that [Cu(R₂[14]aneN₆)]²⁺ can be encapsulated in the supercages of zeolite NaY by in situ template condensation between pre-entrapped Cu(en)₂²⁺ complexes and the corresponding formaldehyde and amine. This strategy appears to be effective for the encapsulated of metal complexes with 14-membered hexaaza macrocycle ligands derived from [Cu(en)₂]²⁺-NaY, as in situ one-pot template condensation in the supercage is still possible and no unreacted [Cu(en)₂]²⁺ ions was detected. Furthermore, the spectroscopic data suggest that the encapsulated complexes do not experience extensive distortions in the supercage and that chemical ligation to the zeolitic surface is minimal. Encapsulated complexes yield mainly THF-2-ol and insignificant amount of THF-2-one, while with their homogenous counterparts, selectivity's to THF-2-one are higher.

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Table 4

Substrate conversions and product selective in the oxidation of THF with H₂O₂ in the presence of encapsulated of copper(II) complexes with 14-membered hexaaza macrocycles

Catalyst	Conversion	THF-2-one	THF-2-ol	2,3-Dihydroxy tetrahydrofuran
6	13.7	56.3	39.1	4.6
7	41.6	64.5	30.2	5.3
8	47.5	47.0	49.6	3.4
9	67.6	29.5	67.6	2.9
10	69.6	28.8	68.4	2.8
11	74.5	27.7	69.5	2.8
12	99.6	19.3	78.4	2.3

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