Redox properties of copper oxinate complexes in zeolite matrices

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Abstract

Bis(8-hydroxyquinoline)copper(II) (Cu-Qn) complex was encapsulated in various zeolites(NaX, NaY, KL, Na-ZSM-5, Naβ, and MCM-41). Redox properties were studied using cyclic voltammetry and correlated with physical properties of various zeolites. The position of HOMO and LUMO level of neat and complex encapsulated in ten and twelve membered ring clusters were calculated using Density Functional Theory(DFT). The HOMO and LUMO level of Cu-Qn increases upon encapsulation in the clusters. Substitution of heteroatom stabilizes the HOMO and LUMO levels compared to pure silicious systems.

1. Introduction

During the last two decades, studies on the isolation, characterization and catalytic activity of transition metal complexes encapsulated in various zeolites have received considerable attention because of their specific catalytic applications when compared to homogeneous complexes [1]. The heterogenization process provides a rigid framework to the metal complex inside the zeolite due to spatial restrictions, Columbic interactions and/ or covalent bonding. It also facilitates the reactions to occur under mild experimental conditions [2]. Encapsulation of metal complexes in zeolites alters the redox properties. Due to these features, the transition metal complexes encapsulated in various zeolites resemble to a certain extent to the enzymes where the catalytic active centers might be a transition metal ion and the protein sheath provides the stability and steric constraints. Inorganic complexes encapsulated in such constrained environments can therefore be termed as zeozymes [3].

Enzymes promote redox reactions in regio- and stereo- specific manner. Selectivity is imposed in natural systems by virtue of alteration of the redox potentials of metal complexes in various protein mantles [4] (Fig 1). As in the biological systems, one can impart the selectivity to metal complexes through alteration of redox potentials by encapsulating them in various zeolites. By knowing the redox potential of metal complexes in various zeolites, one can choose an appropriate system for a particular reaction. Probably due to the complexity of these systems, not all questions regarding the alteration of redox potential of metal complexes both in biological systems and zeozymes have been adequately addressed.

It is possible to correlate the redox potential of metal complexes with various properties of zeolites [5]. This paper describes the encapsulation of bis(8-hydroxy-quinoline)copper(II) (Cu-Qn) in various zeolites (NaX, NaY, KL, Na-ZSM-5, Naβ, and MCM-41). Redox properties were studied using cyclic voltammetry. In order to examine the nature of metal complexes at molecular level, theoretical calculations were performed in various zeolites using Density Functional Theory (DFT).

2. Experimental

Copper exchanged zeolites are prepared according to the method given in literature[6]. Copper oxinate (Cu ($C_{18}N_2O_2H_{12}$) (Cu-Qn) complex was encapsulated in the zeolite matrix by the flexible ligand method [7]. These intrazeolite complexes were characterized by TGA(Perkin Elmer TGA 7),

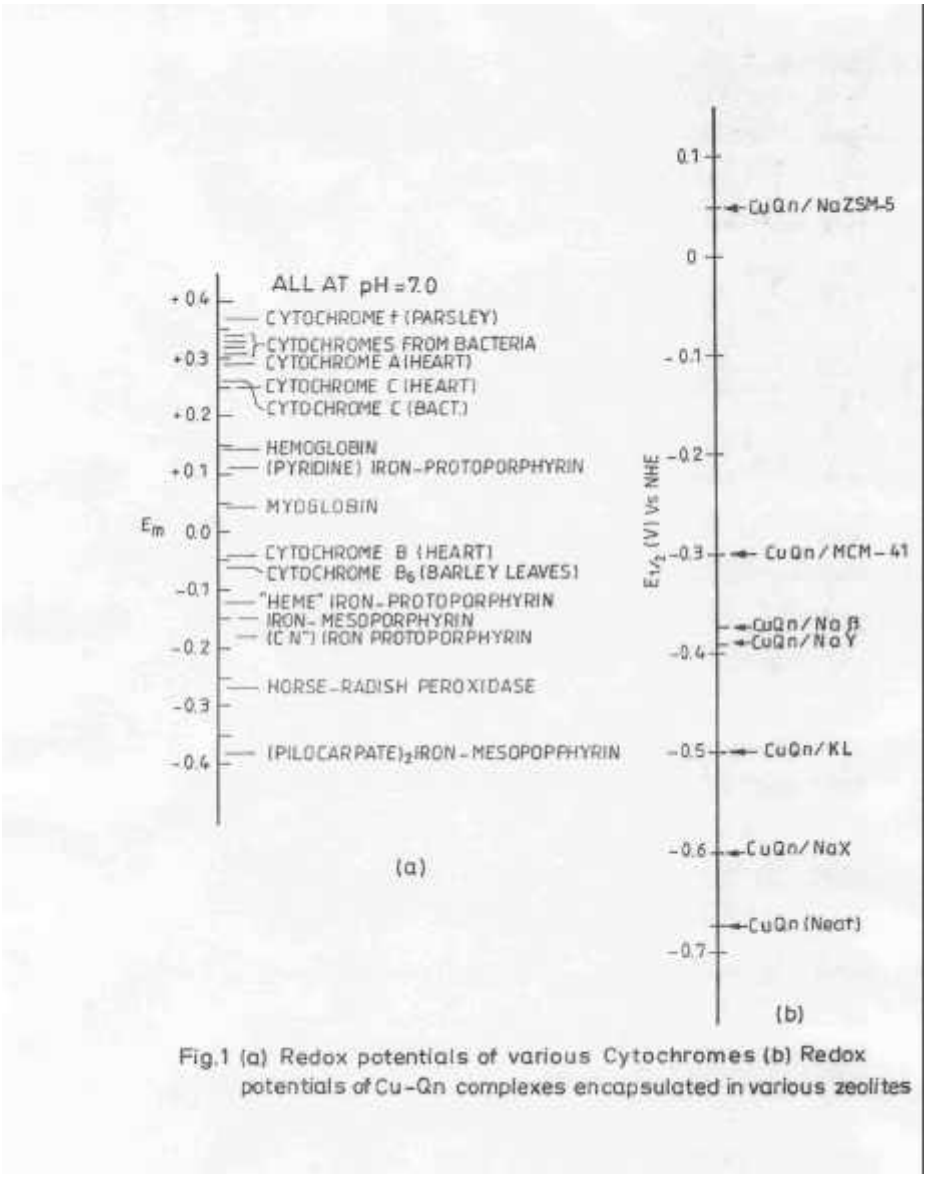


Fig.1 (a) Redox potentials of various Cytochromes (b) Redox potentials of Cu-Qn complexes encapsulated in various zeolites

IR(Perkin Elmer), UV-Vis(Perkin Elmer Lamda 17 UV-Vis spectrometer) and EPR spectroscopy. Electro chemical properties of neat and encapsulated complexes were studied using Wenking-potentio scan (POS73) with digital 2000 X-Y recorder with 25mV/sec as scan rate.

All electrochemical measurements were made using a cell consisting of the Pt foil ($1cm^2$) counter electrode and Ag/AgCl electrode as the reference electrode and grains of neat and encapsulated complexes adhered to glassy carbon as working elctrode in 0.1M KCl.

3. Computational details

The DFT calculations reported in this paper have been carried out using the Gaussian 94 program. All DFT calculations were carried out using Becke three parameter hybrid function with the LYP correlation function (B3LYP) [8] and an effective core potential basis set LanL2DZ [9]. The geometry of neat Cu-Qn complex was optimized at LanL2DZ level. Clusters of ten ($Si_{10}O_{10}H_{20}$)($D_{10}h$ symmetry) and twelve ($Si_{12}O_{12}H_{24}$)($D_{12}h$ symmetry) with 40 and 48 atoms respectively were used for the

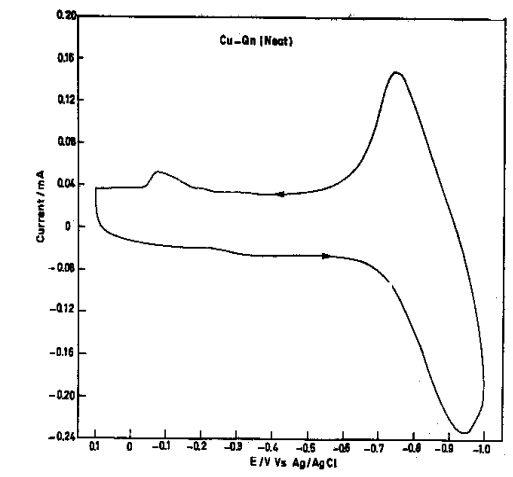
simulations, where the valences of silicon atoms have been saturated with hydrogen atoms. The optimization of geometry has been obtained by using Universal Force Field approach (UFF 1.02). In a typical calculation method, the copper oxinate complex was placed at the center of ten(Si_{10}) and twelve(Si_{12}) membered ring cluster and geometry was optimized by Universal Force Field approach. Advantages of UFF [10] include the fact that it uses a `first-principles approach', where the atomic parameters are based only on the element, its hybridization and its connectivity. Another advantage is that UFF includes metallic elements such as copper, allowing modeling of metal complexes. A third advantage is that UFF is free from *molecule-specific.* Cerius2 software has been used for Force Field calculations. Using force field optimized parameters, DFT calculations have been done at B3LYP/ LanL2DZ level. Similar procedure was used to obtain force field optimized geometries with different Al content.

Table 1
Electro chemical data for neat and encapsulated Cu-Qn complexes

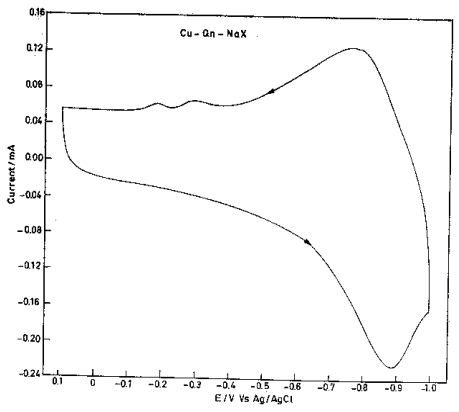
Catalyst	E_{pa} (mV)	E_{pc} (mV)	$E_{1/2}$ (mV)
Cu-Qn	-740[a]	-940	-840
Cu-Qn-NaX	-770	-870	-820
Cu-Qn-NaY	-550	-680	-615
Cu-Qn-KL	-610	-820	-715
Cu-Qn-Naβ	-390	-790	-590
Cu-Qn-NaZSM-5	0	-330	-165
Cu-Qn-NaMCM-41	-330	-690	-510

4. Results and discussion

IR spectra of neat complex shows bands between 1300-1600 cm^{-1} which correspond to C=C and C=N stretching frequency of copper oxinate complex. Similar bands are observed for intrazeolite complex. It suggests that same complex is formed inside the zeolite matrix. UV-Vis spectra of neat and encapsulated complex show bands between 260-410 nm confirming the formation of same complex inside the zeolite matrix.



(a)



(b)

Fig 2. Cyclic voltammogram of (a) Cu-Qn (b) Cu-Qn-NaX.

Figure 2 shows the cyclic voltammogram of the Cu-Qn-NaX and Cu-Qn complex in the potential ranges-1 to 0 V. The voltammogram of neat complex shows a couple of peaks observed at $E_{1/2}$ –840 mV (Table.1). Upon encapsulation in various zeolites, redox potential of Cu-Qn complex is shifted to more positive values. It suggests that oxidizing power of the complex is increased upon encapsulation. The axial coordination with zeolite hydroxyl group may deplete the electron density around the metal site and shift the redox potential of the metal complex towards more positive values. Cyclic voltammetric peaks are getting broadened for encapsulated Cu-Qn in various zeolites. This suggests that encapsulated complexes have

Table 2
Optimized parameters for neat and encapsualated complexes

Catalyst	Cu-O_1	Cu-N_1	Cu-O_2	Cu-N_2	<N_1-Cu-O_1	<N_2-Cu-O_2	<N_2-Cu-O_1	<N_1-Cu-O_2
Cu-Qn-XRD	1.93	1.97	1.93	1.97	84.50	84.80	94.90	95.80
Cu-Qn DFT OPT	1.96[a]	1.98	1.96	1.98	84.62[b]	84.62	95.37	95.37
Cu-Qn-UFF OPT	1.92	1.96	1.92	1.96	86.91	86.91	93.09	93.09
Cu-Qn-Water	2.01	2.01	2.01	2.01	83.78	83.78	96.21	96.21
Cu-Qn-Si_{10}	1.86	1.89	1.86	1.89	94.96	94.96	117.05	117.05
Cu-Qn- $AlSi_{10}$	1.86	1.90	1.86	1.90	94.74	94.71	116.97	118.73
Cu-Qn- Si_{12}	1.87	1.88	1.87	1.88	95.58	95.58	117.42	117.42
Cu-Qn- $AlSi_{12}$	1.87	1.88	1.87	1.88	95.65	95.65	117.18	117.18
Cu-Qn- BSi_{12}	1.86	1.88	1.86	1.88	95.61	95.61	117.55	117.68
Cu-Qn- $GaSi_{12}$	1.86	1.88	1.86	1.88	95.63	95.63	117.07	118.12

[a] distance in angstroms.
[b] angle in degrees.

altered different redox potential values in various positions of zeolite matrix. Because of the partial covalent character of the aluminosilicate crystals, electrons are not localized on the framework atoms rather they are partially delocalized [11]. When a metal complex interacts with an active site, it will perturb all the active sites present within the zeolite, so that complex will have different interaction energy and altered redox potential at different places of zeolite. As in the biological enzymes, redox potential of same Cu-Qn complex is shifted when it is encapsulated in different zeolites(Fig 1).

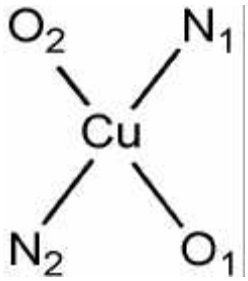


Fig 3. Representation of Cu-Qn

4.1.Theoretical methods

The redox potential of metal complex is altered in various zeoites due to change in the position of HOMO and LUMO level of metal complexes. In order to understand the position of HOMO and LUMO level of metal complexes in various zeolites, theoretical calculations were carried out using Density Functional Theory. The optimized parameters for neat and encapsulated complexes (Fig 3) are given in Table 2. As can be seen from the values given in table 2 both DFT optimization as well as force field optimization of neat Cu-Qn molecule are able to predict the structure of the neat complex quiet reasonably. The neat complex is having a C_2h symmetry. On encapsulation in ten and twelve membered ring systems, it deviates from square planarity(C2h→C2)(Fig 4). The bond length between metal and ligand molecule decreases upon encapsulation. Quantum chemical calculations have proven that Si-O bonds in zeolites have a clear covalent character [12]. Valence electrons in zeolites are distributed all over the framework atoms as a partially delocalized electronic cloud. At relatively short distances between the complex molecule and walls of the zeolite cavities, the electron-electron repulsions will be operative [13] because of which the bond length between copper and ligand molecule decreases.

The HOMO value for neat complex is at -5.36 eV and main contribution to HOMO wave function is coming from p orbital of carbon (31.35%) and nitrogen p orbital

(63.83%) (Table 4). Upon axial coordination of Cu-Qn with water the HOMO value is shifted to less negative value (by 0.49eV). The binding energy of HOMO and LUMO orbitals of the neat complex as well as that of the complex encapsulated in each cluster are given in Table 3. In the case of encapsulated complexes HOMO and LUMO were considered which has main contribution from metal complexes. It is clear that encapsulation of copper oxinate in ten or twelve membered ring systems produce a large shift of HOMO and LUMO energy towards more positive value (by 0.5eV).

Table 3
The HOMO and LUMO values for neat and encapsulated complexes

Catalyst	HOMO(eV)	LUMO(eV)
Cu-Qn-DFTOPT	-5.36	-2.09
Cu-Qn-UFFOPT	-5.29	-2.15
Cu-Qn-Water	-4.87	-1.51
Cu-Qn-Si_{10}	-4.86	-1.69
Cu-Qn- $AlSi_{10}$	-5.21	-2.11
Cu-Qn- Si_{12}	-4.88	-1.61
Cu-Qn- $AlSi_{12}$	-5.08	-1.98
Cu-Qn- BSi_{12}	-5.03	-1.96
Cu-Qn- $GaSi_{12}$	-5.14	-2.11

The type of interaction normally considered when the metal complex is encapsulated inside the zeolite is the following [14]:

(i) Coluombic effects: these are produced by the charge distribution along the framework owing to the partial ionic character of the ionic crystals. This charge distribution generates strong columbic field on the cavities, which might alter the energy level of metal complexes as well as influence the chemical behavior of the transition metal complexes.

(ii) Coordination effects. These are produced by Lewis acid-base type interactions among the transition metal complexes and certain sites of the frame work in the cavity. Weak electron interactions account for the forces of VanderWalls type.

(iii) Double layer effect. Zeolite framework is anionic in nature. When the transition metal complex enters the zeolite cavity it forms a double layer in the zeolite

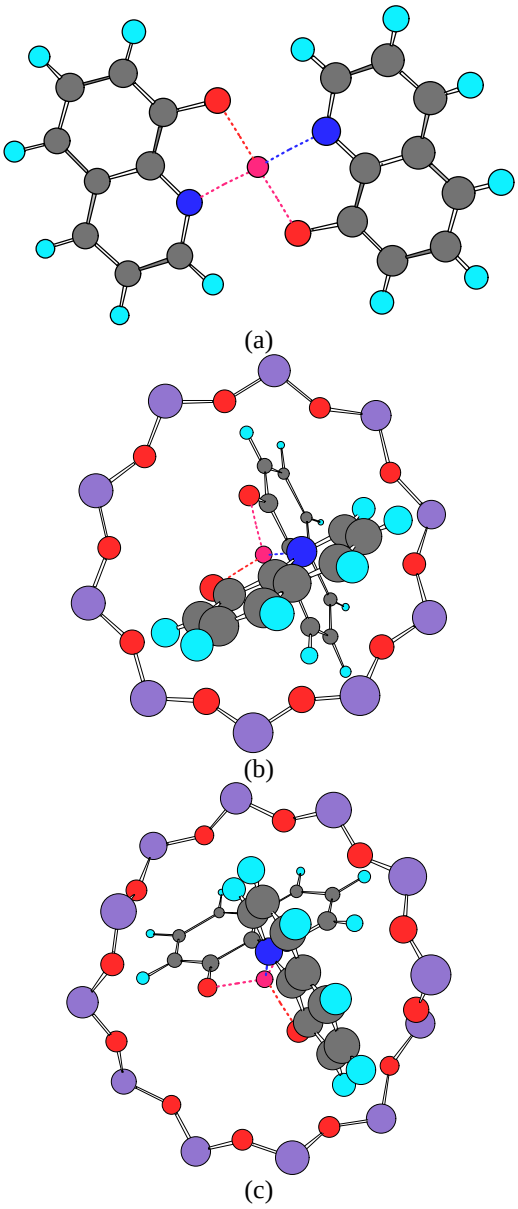


Fig 4.(a) Cu-Qn (b) Cu-Qn-Si_{10} (c) Cu-Qn-Si_{12}

cavities. It is known in the literature that electric field existing in between a double layer is around 10^8V/cm[15]. This electric field alters the energy levels as well as chemical behavior of the transition metal complexes. The percentage orbital contribution of each atomic orbital to HOMO and LUMO are given in Table 4. The p orbitalparticipation of the carbon atom to HOMO decreases after encapsulation. This shows that the molecular orbital of metal complex cannot extend over the entire space

Table 4.
Percentage atomic orbital contributions to HOMO and LUMO level of Cu-Qn and Cu-Qn-Si_{12}

Catalyst	Si		O_{zeo}		H_{zeo}	Cu			$O_{complex}$		N		C		H_{com}
	s	p	s	p	s	s	p	d	s	p	s	p	s	p	s
Cu-Qn															
HOMO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.97	0.00	31.35	0.00	2.85	0.00	63.83	0.00
-5.36 eV															
LUMO	0.00	0.00	0.00	0.00	0.00	0.00	2.26	0.00	0.00	0.91	0.00	20.03	0.00	76.80	0.00
-2.09 eV															
Cu-Qn-Si_{12}															
HOMO	0.13	0.30	0.09	0.24	0.10	0.00	0.38	8.85	0.09	32.83	0.71	4.35	1.44	50.42	0.07
-4.88 eV															
LUMO	0.31	0.65	0.20	0.66	0.24	0.09	0.42	1.06	0.05	2.36	0.08	21.60	0.26	71.96	0.06
-1.61 eV															

and restricts with in the dimension of the zeolite cage. Upon substitution of aluminium in ten and twelve membered ring systems both HOMO and LUMO level of copper oxinate are stabilized compared to pure silicious cluster model. The presence of Bronsted sites change the electrostatic potential generated inside the cage. In a purely silicious zeolite, this negative electrostatic potential will give rise to repulsive interaction on the electrons in the complex and increases the energy levels. If aluminum is introduced, the change $O^{2-} \rightarrow OH^-$ will alter the electrostatic potential less negative due to proton shielding on the corresponding oxide ion and thus decreases the electrostatic repulsion potential. Therefore when aluminium is introduced in the zeolites the HOMO and LUMO levels of metal complexes get stabilized compared to purely silicious zeolites. In order to know whether this stabilization is due to aluminium or not, other trivalent atoms are substituted(B,Ga) in twelve membered ring systems and Cu-Qn complex was encapsulated in this modified cluster. The HOMO and LUMO values of the Cu-Qn complex in this modified cluster is given in Table 3. Both HOMO and LUMO of Cu-Qn are stabilized in trivalent ion substituted systems compared to the purely silicious zeolite. It shows that aluminium or other trivalent ions may not be responsible for stabilization of HOMO and LUMO levels of metal complexes. The total energy of silicious and other trivalent ion substituted clusters are given in Table 5. The stabilization energy for the formation of the cluster computed as the difference in the total energy of the cluster and the sum of the total energy of the individual atoms that constitute the cluster are given in Table 4. The stabilization energy of trivalent ion substituted system is lower than that of the pure silicious zeolites (Table 3). It shows that structure of the cluster is not responsible for the stabilization of HOMO and LUMO level of metal complexes. The generation of charge compensating cation reduces the electric field acting inside the cavity that stabilizes the HOMO and LUMO level of metal complexes. Upon aluminium substitution, the HOMO value of ten membered ring system is more stabilized compared to that of twelve membered ring system. This is in accordance to the redox potential measurements where redox potential of Cu-Qn in NaZSM-5 is shifted towards more positive value compared to that of NaX and NaY. In neat complex two water molecules are occupying the axial position. Comparing the HOMO value of Cu-Qn in aluminium substituted cluster with that of Cu-Qn-H_2O, the HOMO value of Cu-Qn is stabilized more in aluminium substituted cluster compared to that of Cu-Qn-H_2O. This is supported by experimental observations (refer Table 1) where redox potential of copper oxinate in various zeolites is shifted towards more positive values compared to that of neat complex.

Table 5
Total energy and stabilization energy of heteroatom substituted cluster

Catalyst	Total energy(eV)	Stabilization energy (eV)
Si_{12}	-26238.17	-1569.47
BSi_{11}	-26823.67	-1543.89
$AlSi_{11}$	-26202.09	-1521.58
$GaSi_{11}$	-26203.18	-1522.67

5. Conclusions:

Bis(8-hydroxyquinoline)Copper complex was encapsulated in NaX, NaY, KI, MCM-41, Naβ and NaZSM-5 zeolites. Alterations in redox properties of zeolite encapsulated complexes can be accounted for on the basis of physical properties of zeolites employed. Theoretical calculations show that the energy values of HOMO and LUMO levels are shifted towards less negative value on encapsulation of Cu-Qn complexes. Increasing Al content at the ten and twelve membered ring clusters stabilizes both HOMO and LUMO energy levels of metal complexes. This may be due to decrease of electrostatic field inside the zeolite matrix.

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